A MECHANISTIC INVESTIGATION OF P-XYLENE AND WATER VAPOR SORPTION ON SOILS AND CLAY MINERALS

By

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Abstract of Dissertation Presented to the Graduate School
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Vapor-phase sorption of p-xylene and water on soils and clay minerals was studied using a flow-equilibration technique that allowed the amount of sorbed water and p-xylene to be measured independently. Oven-dry sorbents exhibited a sizable capacity to adsorb p-xylene vapors which was strongly correlated to sorbent surface area. Increasing the relative humidity to 67 and 90% resulted in dramatic reductions in p-xylene sorption and a shift from Type-II to Type-III adsorption isotherms, regardless of the organic carbon content of the sorbent. The observed increase in p-xylene sorption above relative vapor pressures of 0.6 suggests that hydrated sorbents can sorb significant quantities of organic vapors near the contaminant source. Similar results were obtained for the sorption of p-

xylene vapors on quartz sand using a gas chromatographic technique, which provided an efficient and versatile alternative to batch methods.

At relative humidities above which the sorbent surface was covered by at least a monomolecular layer of water, p-xylene sorption by Webster soil was primarily attributed to partitioning into organic carbon. However, predictions of the surface excess based on the Gibbs equation indicated that essentially all p-xylene sorption on sorbents of low organic carbon content was due to adsorption at the gas-liquid interface. Therefore, it is recommended that vapor-phase sorption be described by a multi-mechanistic model that incorporates adsorption onto exposed mineral surfaces, adsorption at the gas-liquid interface, dissolution into adsorbed water films, and partitioning into organic carbon.

The effect of cation saturation on the adsorption of water and p-xylene vapors from single- and binary-vapor systems was also investigated. Water and p-xylene adsorption on Ca- and Na-saturated kaolin was directly related to the hydration energy of the exchangeable cation. However, Li-saturated kaolin exhibited reduced adsorption which was attributed to a decrease in total charge after heating. Therefore, Li-kaolin is not recommended as a reference surface for the study of vapor-phase sorption. Predictions of the competitive adsorption of water and p-xylene vapors using two-component Brunauer, Emmett, and Teller models indicated that the preferential adsorption of water from p-xylene-water systems was the result of cation hydration effects.

CHAPTER 1
INTRODUCTION

Vapor-Phase Sorption

The widespread detection of volatile organic chemicals (VOCs) in groundwater and soil has prompted intensive study of vapor-phase sorption and transport in porous media. Contaminants of this nature, such as petroleum-based solvents, frequently enter the environment as a result of improper disposal techniques, accidental spills, and loss from storage tanks. The subsequent distribution and mobility of VOCs in the unsaturated zone can be directly influenced by vapor-phase sorption. Previous studies have demonstrated that anhydrous soils and clays have a sizable capacity to adsorb organic vapors, but this capacity is greatly reduced in the presence of water (Call, 1957; Chiou and Shoup, 1985; Rhue et al., 1989). However, a comprehensive understanding of the processes responsible for VOC sorption in the unsaturated zone has yet to be attained. This is particularly true for soils at high relative humidity (RH), at which time a number of mechanisms may contribute to organic vapor retention, including dissolution into adsorbed water films, partitioning into organic carbon (OC), and adsorption at gas-liquid-solid interfaces.

Adsorption on Oven-Dry Sorbents

The adsorption of vapors on oven-dry sorbents has been studied in detail, and provides a basis from which to investigate adsorption in more complex systems. In his classic treatise on vapor-phase adsorption, Brunauer (1943) defines adsorption as the accumulation of a chemical species from one bulk phase at the surface of another bulk phase, without penetrating the structure of the second phase. Based on the nature of adsorbate-adsorbent interactions, adsorption can be classified as either physical or chemical (Table 1-1). The adsorption of nonpolar organic vapors on mineral surfaces is generally considered to result from nonspecific molecular interactions, such as van der Waals forces, which are also responsible for vapor condensation and deviations from ideal behavior. Chemical adsorption of aromatic hydrocarbons has been observed on Cu-saturated montmorillonite using infrared and ultraviolet-visible spectroscopy (e.g., Pinnavaia et al., 1974; Pinnavaia and Mortland, 1971). It was postulated that the chemisorbed species was coordinated with exchangeable Cu(II) ions via π electrons. However, interactions of this nature are typically limited to clay minerals saturated with certain transition metals under anhydrous conditions.

The equations of Freudlich, Langmuir, and Brunauer, Emmett, and Teller (BET) are frequently used to interpret gas-solid adsorption data. Although the Langmuir and BET models can be derived theoretically, the Freudlich adsorption model is based solely on the following empirical equation:

$$S = kP^{1/n} \qquad (1\text{-}1)$$

Table 1-1. Comparison of physical and chemical adsorption of vapors on solids.

Property	Physical Adsorption	Chemical Adsorption
Enthalpy of Adsorption	≤ 80 kJ/mole	≥ 200 kJ/mole
Reversibility of Adsorption	Reduction in vapor pressure results in desorption.	Stronger treatment required for desorption. Desorption may result in chemical alterations.
Adsorbed Layers	Multilayer formation.	Limited to monolayer.
Adsorption Rate	Instantaneous. May be limited by diffusion.	Rapid or slow. May require activation energy.
Adsorbate-Adsorbent Interaction	Nonspecific. Van der Waals forces.	Specific. Chemical bond formation.

where S is the amount adsorbed (mg/g), P is the equilibrium vapor pressure, and k and n are constants. The constants k and n are indicative of the extent and intensity of adsorption, respectively. At low vapor pressures the value of n frequently approaches one, which results in a linear isotherm. However, the Freudlich equation rarely fits gas-solid adsorption data over a range of vapor pressures.

The Langmuir model was the first theoretical treatment of adsorption, and has been applied with reasonable success to systems exhibiting chemical adsorption. At equilibrium, Langmuir (1916) considers the rate of evaporation (desorption) from occupied sites to be equal to the rate of condensation (adsorption) on the bare surface, which yields the following equation:

$$\frac{S}{S_m} = \frac{K P}{1 + K P} \qquad (1\text{-}2)$$

where S is the amount adsorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), P is the equilibrium vapor pressure, and K is the rate of adsorption divided by the rate of desorption. The Langmuir adsorption isotherm is linear at low vapor pressures and reaches a limiting value at or above vapor pressures corresponding to monolayer coverage (Figure 1-1a).

Implicit in the kinetic derivation of the Langmuir equation are the following assumptions: (1) the adsorbate behaves as an ideal gas in the bulk phase; (2) adsorption is limited to monolayer coverage; (3) the energy of adsorption is constant; (4) no adsorbate-adsorbate interactions occur; (5) adsorption is localized

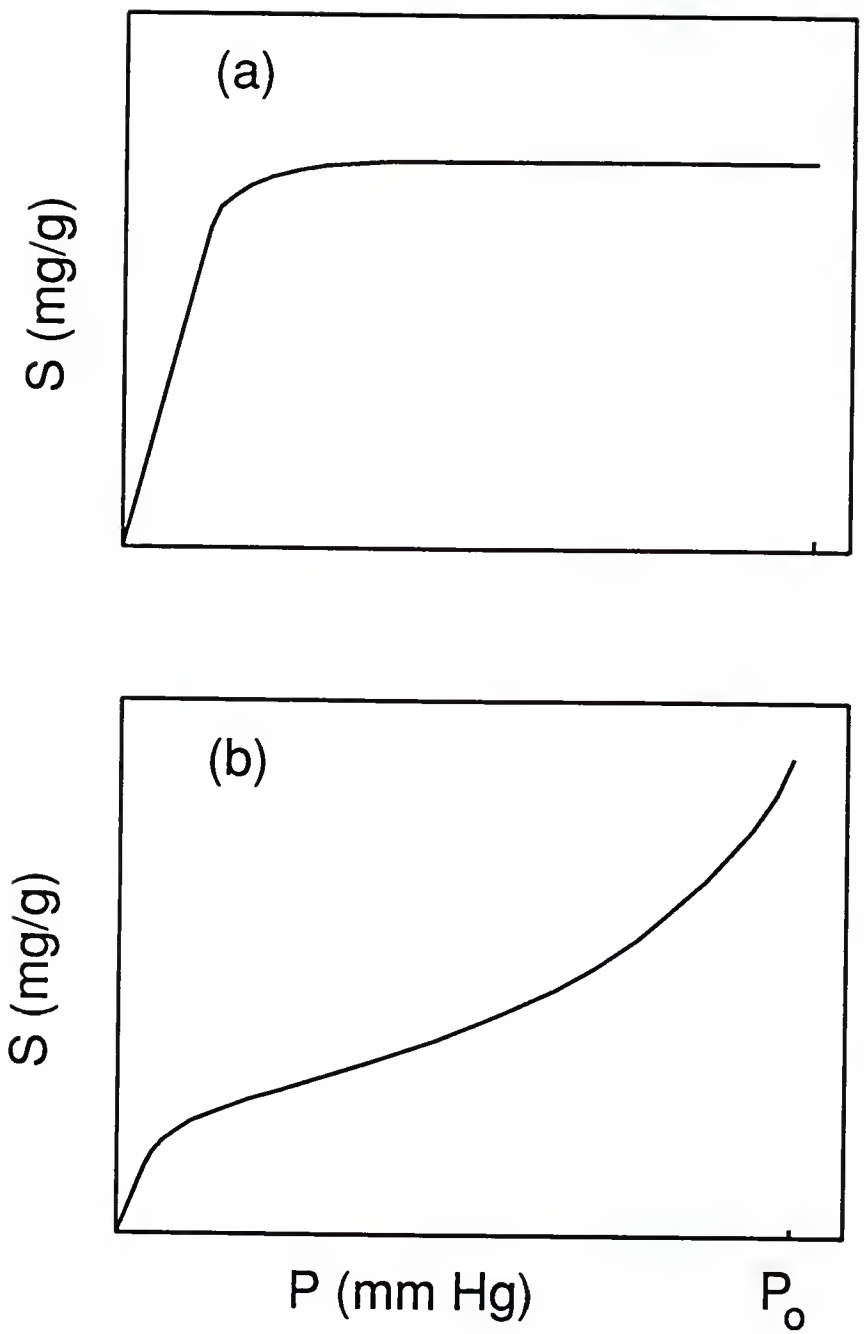

Figure 1-1. Gas-solid adsorption isotherms characteristic of the (a) Langmuir model (Type I) and (b) BET model (Type II).

(i.e., site-specific). The assumption of constant adsorption energy and the absence of adsorbate-adsorbate interactions are rarely valid (Ross and Olivier, 1964). However, the errors associated with these assumptions tend to nullify one another, and thus the success of the Langmuir equation may be attributed, in part, to this coincidence.

Brunauer, Emmett, and Teller (BET) extended the Langmuir model to account for multilayer adsorption by assuming that the Langmuir equation is applicable to each adsorbed layer (i.e., each layer has a fixed number of adsorption sites). The first layer is assumed to have a heat of adsorption equal to Q_1, while all successive layers have heats of adsorption equivalent to the heat of vaporization (Q_v). Adsorption and desorption are considered to occur only from exposed surfaces, and at equilibrium the amount of solute adsorbed on each layer is at steady state. The BET equation is given as follows:

$$\frac{S}{S_m} = \frac{C(P/P_o)}{(1-P/P_o)\,[1-P/P_o+C(P/P_o)]} \qquad (1\text{-}3)$$

where S is the amount adsorbed (mg/g), S_m is the monolayer adsorption capacity (mg/g), P is the equilibrium vapor pressure, P_o is the saturated vapor pressure, and C is a parameter related to the heat of adsorption. The BET equation typically yields Type-II adsorption isotherms which are characteristic of multilayer formation resulting from physical adsorption (Figure 1-1b).

The values of S_m and C can be obtained from a least squares fit of adsorption data to the linear form of the BET equation, given as follows:

$$\frac{P/P_o}{S(1-P/P_o)} = \frac{1}{S_mC} + \frac{(C-1)P/P_o}{S_mC}. \qquad (1\text{-}4)$$

Estimated values of S_m and C for a range of adsorbate-adsorbent systems are presented in Table 1-2. In theory, the approximate value of C is given by the following equation:

$$C \approx e^{(Q_1 - Q_v)/RT} \qquad (1\text{-}5)$$

where R is the gas constant and T is the temperature (°K). Provided the heat of vaporization (Q_v) is known, the heat of adsorption (Q_1) can be calculated from the value of C (e.g., Chiou and Shoup, 1985; Jurinak and Volman, 1957). However, Sing et al. (1985) concluded that the C parameter obtained from the BET model does not provide a quantitative measure of heats of adsorption, but does indicate the relative magnitude of adsorbate-adsorbent interactions. In general, the values of C in Table 1-2 are indicative of the low interactions energies associated with physical adsorption. The BET equation is considered to yield reliable estimates of the monolayer adsorption capacity for systems exhibiting Type-II adsorption isotherms. The surface area of the adsorbent can then be calculated from the value of S_m and the cross-sectional area of the adsorbate, typically estimated from the liquid density. This procedure has become standard practice for the determination of surface area from N_2 adsorption isotherms (Adamson, 1982).

Table 1-2. BET parameters calculated from the adsorption of organic vapors on anhydrous soil materials.

Adsorbate	Adsorbent	S_m	C	Reference[a]
		--mg/g--		
Benzene	Parsons silt loam	7.3	1.8	1
Benzene	Weller silty loam	11.3	20.0	1
Benzene	Woodburn silty clay	5.6	13.6	2
Toluene	Bentonite	7.3	10.0	3
Toluene	Kaolin	4.2	27.0	3
Toluene	Silica Gel	65.3	12.0	3
Toluene	Webster silty clay loam	2.3	12.0	3
p-Xylene	Bentonite	7.9	10.0	3
p-Xylene	Kaolin	4.6	18.0	3
p-Xylene	Silica Gel	64.7	17.0	3
p-Xylene	Lula aquifer material	1.8	45.0	3
Ethylbenzene	Bentonite	7.8	17.0	3
Ethylbenzene	Webster silty clay loam	2.6	14.0	3
Dichloropropane	Parsons silt loam	8.2	7.8	1
Dichloropropane	Weller silty loam	12.7	32.7	1
Dichloropropane	Bernow sandy loam	1.2	18.1	1
Dichloropropane	Summit silty loam	8.1	8.1	1
Chlorobenzene	Woodburn silty clay	7.5	22.8	2
m-Chlorobenzene	Woodburn silty clay	7.4	24.4	2
p-Dichlorobenzene	Woodburn silty clay	5.5	78.5	2
1,2,4-trichlorobenzene	Woodburn silty clay	9.5	27.5	2
Ethylene dibromide	Yolo silty clay	35.9	73.4	4
Ethylene dibromide	Yolo loam	18.7	96.2	4
Ethylene dibromide	Salanis clay	23.9	59.9	4
Ethylene dibromide	Meloland clay loam	26.3	41.3	4
Ethylene dibromide	Hanford sandy loam	3.7	15.0	4
Ethylene dibromide	Aiken clay loam	26.9	17.1	4
Ethylene dibromide	Staten peaty muck	11.7	12.6	4

[a] (1) Poe et al. (1988); (2) Chiou and Shoup (1985); (3) Rhue et al. (1988); (4) Jurinak and Volman (1957).

Rhue et al. (1988) reported that adsorption of p-xylene vapors on oven-dry silica gel was considerably greater than that on kaolin, bentonite, and Lula aquifer material (Figure 1-2a). However, when the adsorption data were normalized to the monolayer adsorption capacity (S_m) of each adsorbent, the relative adsorption was essentially the same for all adsorbents studied (Figure 1-2b). A similar trend was observed for the adsorption of ethylene dibromide (EDB) on a number of soils (Jurinak and Volman, 1957). The slight increase in relative adsorption noted for Lula aquifer material corresponded to a larger value of C, suggesting that specific adsorbate-adsorbent interactions may have occurred. However, the overall similarity in relative adsorption is remarkable considering the variation in adsorbent properties, and indicates that the adsorption of organic vapors on mineral surfaces is primarily a function of surface area (Jurinak and Volman, 1957; Rhue et al., 1988).

The significance of the monolayer adsorption capacity obtained from the BET model has recently come under scrutiny. Rhue et al. (1988) suggested that for systems exhibiting low values of C, the coverage of the entire surface with a single monolayer may not occur at any relative vapor pressure. In fact, multilayer adsorption of EDB on Ca-saturated montmorillonite and kaolinite was observed at surface coverages of 0.65 and 0.35, respectively (Jurinak and Volman, 1957). The corresponding values of C for the montmorillonite and kaolinite systems were 24 and 14, respectively. In theory, the onset of multilayer formation prior to monolayer coverage would result in the formation of discrete adsorbate films or

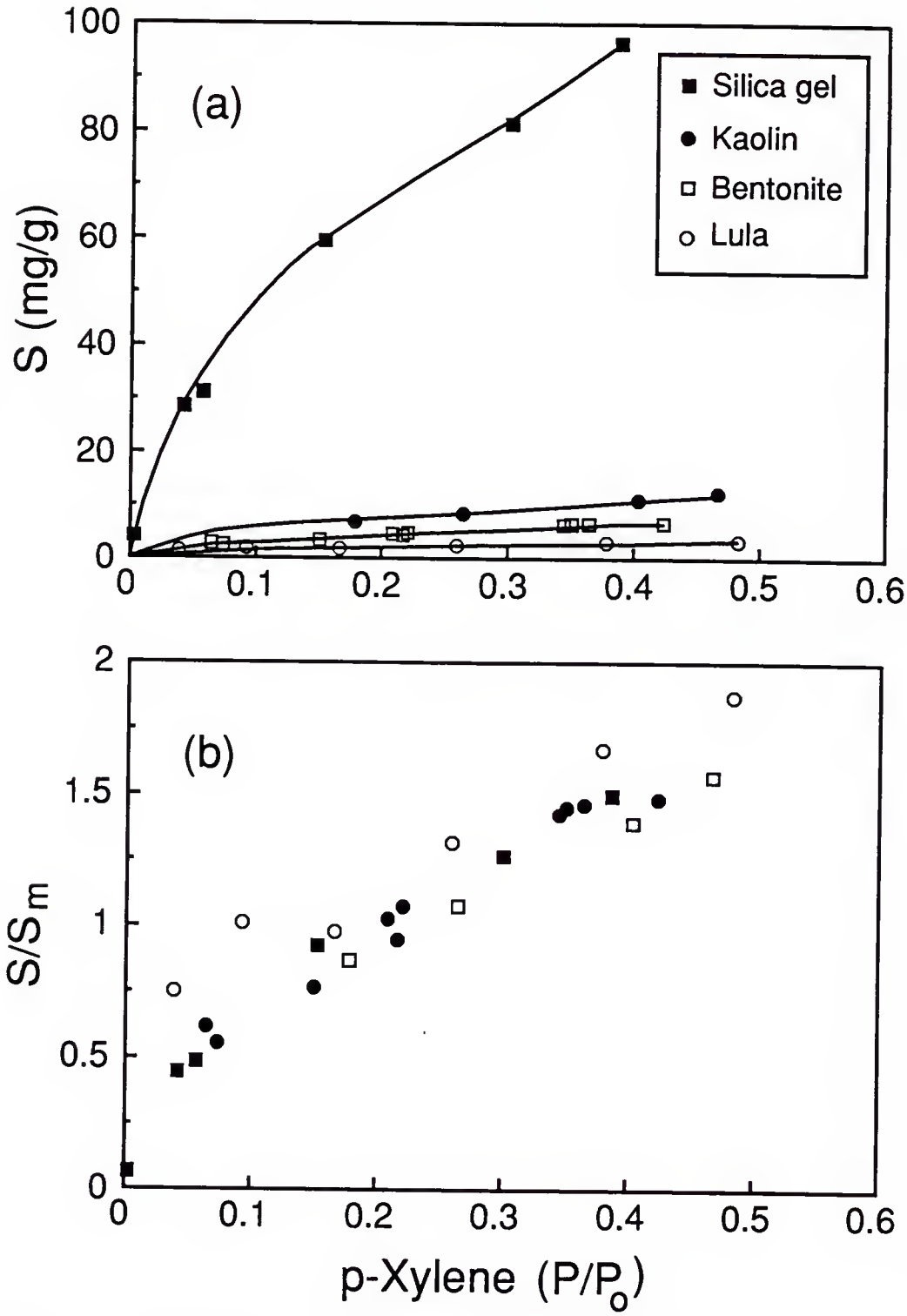

Figure 1-2. Adsorption of p-xylene vapors on oven-dry silica gel, kaolin, bentonite, and Lula aquifer material, expressed as (a) amount adsorbed and (b) relative amount adsorbed, reported by Rhue et al. (1989).

"patches" on the adsorbent surface. This scenario appears to be reasonable for the adsorption of nonpolar organic vapors on mineral surfaces based on the similarity in their heats of adsorption and condensation (Rao at al., 1989).

Competitive Adsorption

Under natural conditions, the adsorption of organic vapors will usually occur on surfaces containing at least some adsorbed water. Chiou and Shoup (1985) reported that the magnitude of water, 1,2,4-trichlorobenzene, chlorobenzene, and benzene adsorption on oven-dry Webster soil was positively correlated to adsorbate polarity (Figure 1-3a). It should be noted that the relative adsorption was similar for all adsorbates studied, which suggests that the monolayer adsorption capacity determined from the BET model accounts for variations in both adsorbate and adsorbent properties (Figure 1-3b). The fact that adsorbate polarity enhanced vapor-phase adsorption indicates that water will compete strongly with organic vapors for adsorption sites. The adsorption of water on mineral surfaces has been attributed to cation-dipole interactions, hydrogen bonding, and weak charge transfer, which fall within the extremes of physical and chemical adsorption (Burchill et al., 1981). Jurinak and Volman (1961b) reported that the enthalpy of water adsorption on Ca- and Ba-saturated kaolin was approximately -120 kJ/mole, which corresponded to an enthalpy of cation hydration of approximately -250 kJ/mole. In contrast, Rao et al. (1989) reported that heats of adsorption for trichloroethene (TCE), toluene, and cyclohexane vapors on oven-dry Oldsmar soil

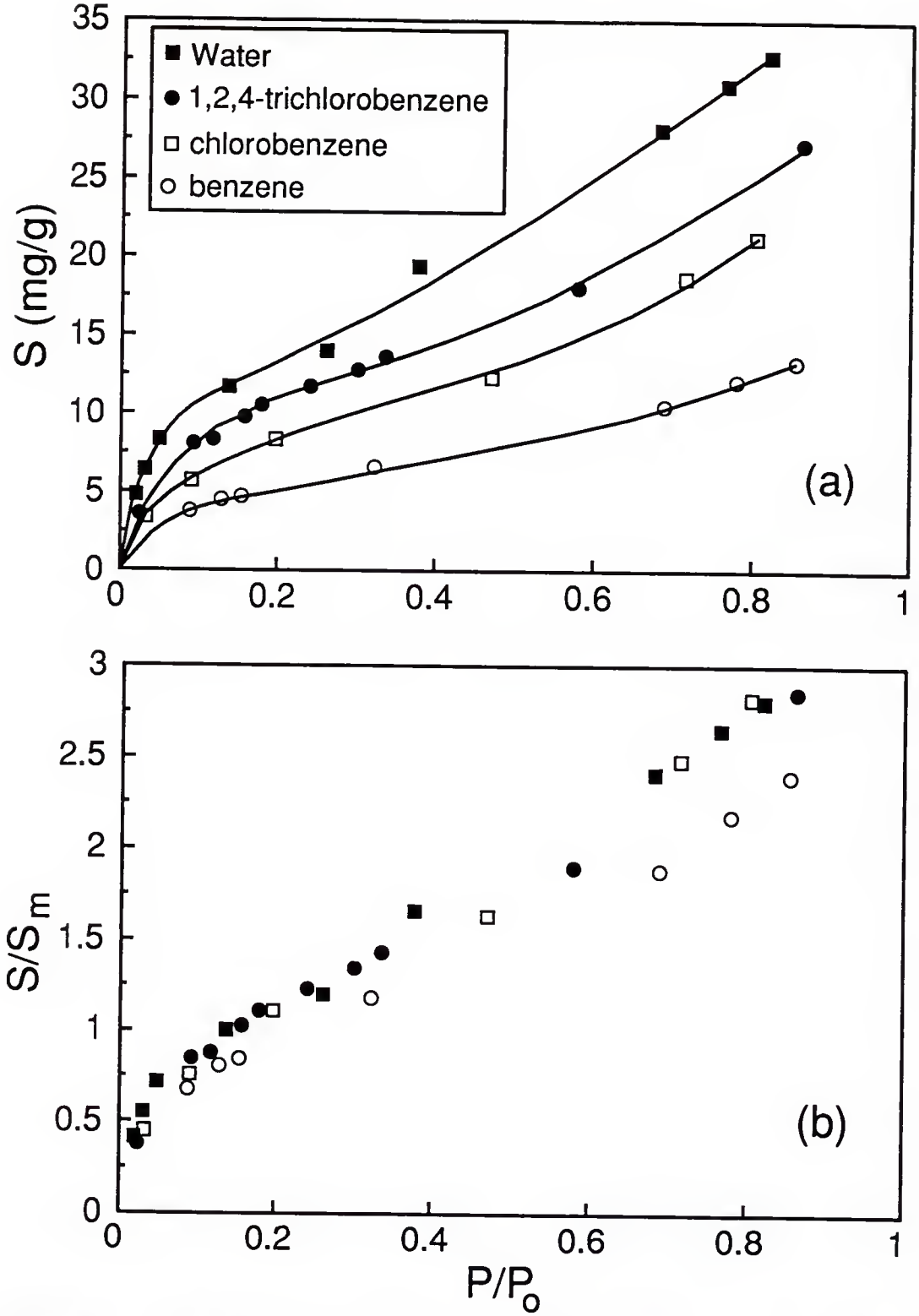

Figure 1-3. Adsorption of water, 1,2,4-trichlorobenzene, chlorobenzene, and benzene on oven-dry Woodburn soil, expressed as (a) amount adsorbed and (b) relative amount adsorbed, reported by Chiou and Shoup (1985).

were -23, -37, and -34 kJ/mole. Thus, as the relative humidity or soil moisture content increases, water will displace organic vapors from adsorbent surfaces resulting in the suppression of VOC sorption. This finding is supported by infrared studies, which have demonstrated that p-xylene was immediately displaced from the surface of montmorillonite when laboratory air was introduced into the sample cell (C. T. Johnston, 1990, personal communication).

Prior to the attainment of monolayer coverage with water, the adsorption of organic vapors may proceed, essentially unhindered, on exposed mineral surfaces. Rhue et al. (1989) reported that p-xylene adsorption on silica gel and kaolin was not suppressed until the RH was greater than that corresponding to the monolayer adsorption capacity determined from the BET model (i.e., RH ≈ 18%) (Figure 1-4). In contrast, Call (1957) observed a substantial decrease in ethylene dibromide adsorption at 5% RH (Figure 1-5). Regardless of the exact point at which competitive effects become evident, these data indicate that the presence of water vapor not only reduces organic vapor sorption, but also results in a shift from Type-II adsorption isotherms to ones that are essentially linear.

In order to predict the competitive adsorption of water and organic vapors on mineral surfaces a two-component adsorption model must be employed. Fortunately, the BET equation has been modified by Hill (1946a, 1946b), and more recently by Rhue et al. (1989), to account for adsorption from two-component systems. The only additional assumption required to derive the equation of Rhue et al. (1989) is that each component adsorbs only onto exposed mineral surfaces

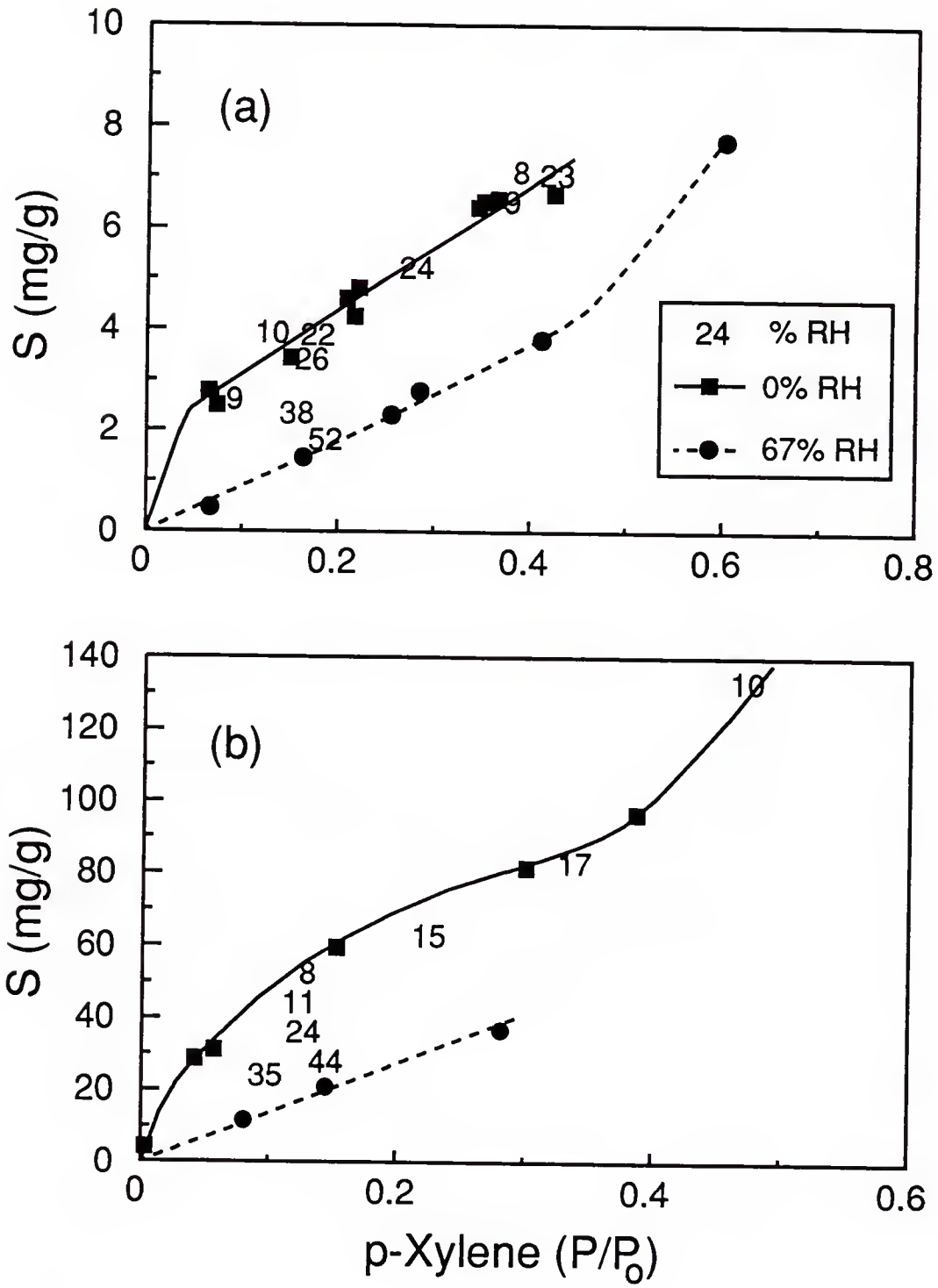

Figure 1-4. The effect of RH on the adsorption of p-xylene vapors on (a) kaolin and (b) silica gel reported by Rhue et al. (1989).

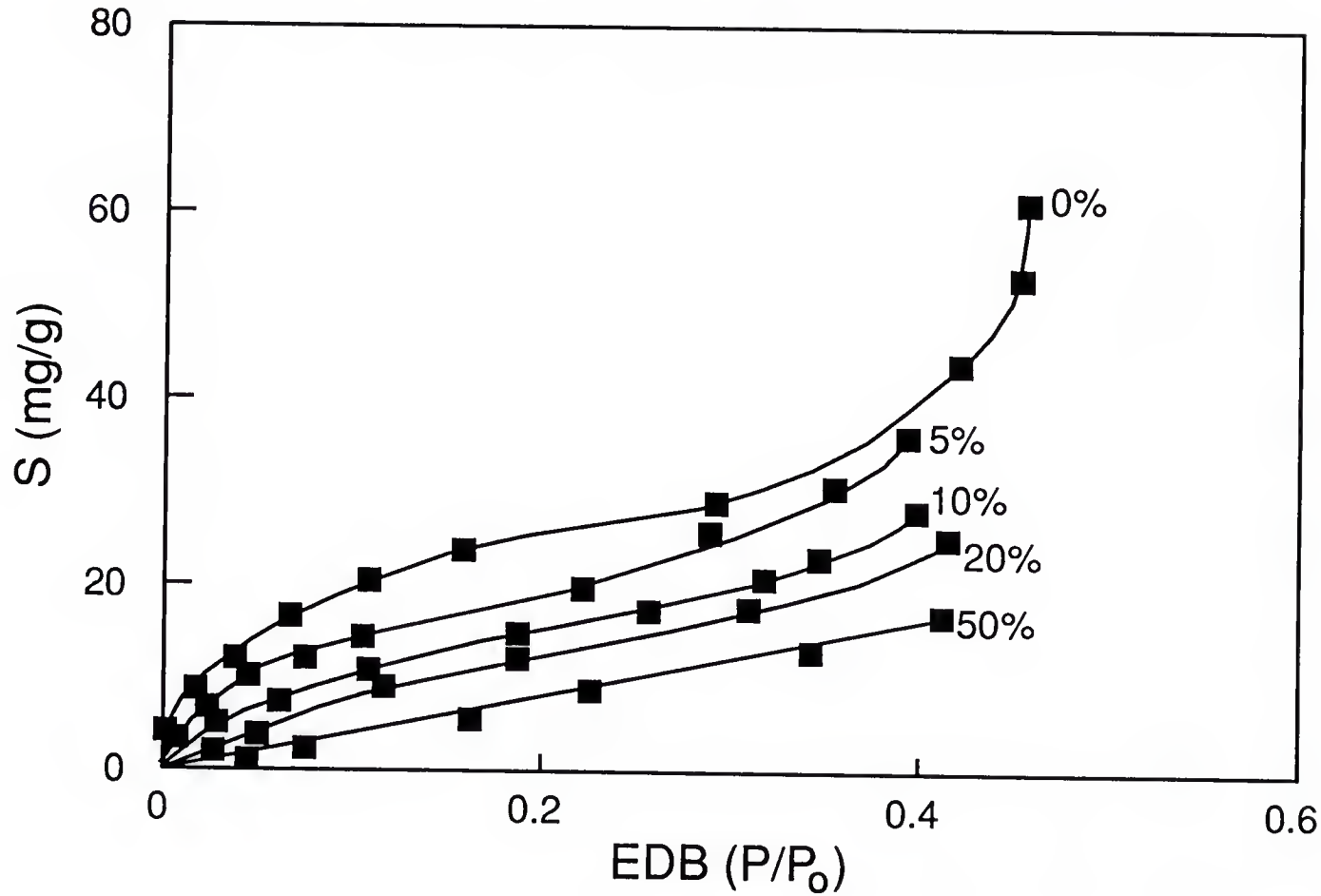

Figure 1-5. The effect of RH on the adsorption of EDB vapors on Whittlesey Black Fen soil reported by Call (1957).

or adsorbed layers of itself. This implies that the two components form immiscible fluids on the surface, which is reasonable for adsorbates of low mutual solubility, such as water and a nonpolar organic vapor. The total adsorbed mass of component "a", M_a (mg/g), can be calculated from the following equation:

$$M_a = \alpha_a C_a S_o [X_a/(1-X_a)^2] \qquad (1\text{-}6)$$

where α_a is the mass of component "a" occupying a unit area of surface (mg/m^2), C_a is the BET parameter related to the heat of adsorption determined from single-component adsorption isotherms, X_a is the relative vapor pressures of component "a", and S_o is the area of bare surface per unit mass of adsorbent (m^2/g). Unfortunately, the value of S_o is unknown in a binary system, and thus the amount of each component adsorbed could not be expressed on a per-mass-of-adsorbent basis (Rhue et al.,1989). However, the two-component model was evaluated by comparing the measured and predicted mass fraction of component "a" (F_a) on the surface using the following equation:

$$F_a = \frac{M_a}{M_a + M_b} . \qquad (1\text{-}7)$$

The multi-component BET equation of Hill (1946a, 1946b) is based primarily on the BET postulate which states that molecules of the second and higher adsorbed layers possess evaporation-condensation properties of the bulk liquid. If this assumption is valid, it follows that adsorption and desorption from the second and succeeding layers of a binary system should approximate the properties of the liquid mixture. In addition, Hill assumed that area fraction of

component "a" (γ_a) is related to the mole fraction (N_a) by the following equation:

$$\gamma_a = \frac{N_a}{N_a + (1-N_a)\,(v_b/v_a)^{2/3}} \qquad (1\text{-}8)$$

where v_a and v_b are the mole fractions of component "a" and "b", respectively. If component "a" is assumed to adsorb only onto bare mineral surfaces and an adsorbed layer of itself, Hill's equation can be reduced to:

$$\frac{S_a}{S_{am}} = \frac{X_a[C_a(1-X_b) + X_bC_b]}{(1-X_a-X_b)\,[1+X_a(C_a-1) + X_b(C_b-1)]} \qquad (1\text{-}9)$$

where S_a is the amount of component "a" adsorbed (mg/g), S_{am} is the monolayer adsorption capacity of component "a" (mg/g), X_a and X_b are the relative vapor pressures of component "a" and "b", respectively, and C_a and C_b are the BET parameters related to the heat of adsorption for component "a" and "b", respectively. The values of S_{am}, C_a, and C_b are determined from single-component adsorption isotherms. If one of the components is absent (i.e., X_a or $X_b = 0$), Hill's equation reduces to the single-component BET equation. Although the derivation referred to here is limited to a two-component system, in theory, the Hill equation can accommodate an infinite number of components.

Due to the lack of suitable adsorption data, the two-component models of Rhue et al. (1989) and Hill (1946a, 1946b) have rarely been tested.

Sorption at High Relative Humidity

At RHs approaching saturation (i.e. RH ≥ 90%), the sorption of organic vapors has been attributed to partitioning into organic carbon (Chiou and Shoup, 1985). This hypothesis is based on (1) the linear nature of benzene and chlorobenzene vapor adsorption isotherms on Woodburn soil at 90% relative humidity, and (2) the similarity in the magnitude of sorbate uptake from the aqueous and vapor phase. However, linear isotherms have been obtained for a range of sorbents, including those with trace levels of organic carbon (OC), such as kaolin, silica gel, and Ca-saturated montmorillonite (Call, 1957; Rhue et al., 1989). In addition, vapor-phase sorption coefficients, normalized for OC (K_{oc}), calculated for sorbents of low OC content have repeatedly been found to be orders of magnitude greater than literature values (Rhue et al., 1989; Peterson et al., 1988). Although these data suggest that other mechanisms may contribute to the vapor-phase sorption at high RHs, the sorption of organic vapors on hydrated soils is widely described by dissolution into adsorbed water films and subsequent partitioning into OC (Baehr, 1987; Glotfelty and Schomburg, 1989; Jury et al., 1990).

The adsorption of insoluble and sparingly-soluble organic vapors has also been investigated by gas chromatography (GC). In general, Type-III isotherms have been obtained for the adsorption of nonpolar vapors on hydrated sorbents, with heats of adsorption that are smaller than heats of vaporization (Dorris and Gray, 1981; Karger et al., 1971a, 1971b). These data suggest that the gas-liquid

interface of adsorbed water films acts as a low energy surface toward nonpolar vapors. Once the surface is covered with several monomolecular layers of water it appears that the sorbent has no effect on vapor-phase adsorption. Karger et al. (1971a, 1971b) concluded that adsorbed water films between 1.5 and 200 nm in thickness have properties similar to bulk water. Measurements of the change in surface tension of bulk water with vapor pressure also indicate that nonpolar organic vapors are adsorbed at the gas-liquid interface (Blank and Ottewill, 1964; Cutting and Jones, 1955; Hauxwell and Ottewill, 1968). Due to the large surface area of adsorbed water films, adsorption at the gas-liquid interface of hydrated soils may contribute significantly to VOC sorption. In fact, Call (1957) attributed the sorption of EDB on moist soils to adsorption at the gas-liquid interface and dissolution into adsorbed water films. It is apparent that a number of mechanisms may contribute to vapor-phase sorption at high RHs, including partitioning into OC, adsorption at the gas-liquid interface, and dissolution into adsorbed water films. In addition, the extent to which sorbate and sorbent properties determine the importance of each mechanism remains largely unknown.

Research Summary

The purpose of this work was to investigate, from a mechanistic perspective, the sorption of organic vapors on soils and clay minerals. The study of soil processes, particularly sorption, is limited by our inability to measure soil phenomena on a microscopic scale. Thus, a macroscopic approach was

employed here, in which experiments were specifically designed to ascertain the mechanism responsible for sorption under various sorbate-sorbent regimes.

A single volatile organic chemical, p-xylene, was utilized in these studies. Although this may be viewed as a limitation, it allowed for intensive study of the factors affecting vapor-phase sorption and for the development of experimental techniques to study VOC sorption. Relevant physicochemical properties of p-xylene are presented in Table 1-3. The sorbents used in these studies were selected to provide a range of physical and chemical properties. In addition, the OC content and cation saturation of certain sorbents were modified in order to study the effect of such treatments on vapor-phase adsorption.

In Chapter 2, a flow-equilibration apparatus was utilized to measure the sorption of p-xylene vapors on soils and mineral surfaces at 0, 67, and 90% RH. Experiments were designed to determine the amount of p-xylene sorption attributable to adsorption at the gas-liquid interface, dissolution into adsorbed water films, and partitioning into OC. Adsorption at the gas-liquid interface of hydrated sorbents was estimated from measurements of the surface tension of bulk water exposed to p-xylene vapors using the Gibbs adsorption equation.

Gas chromatography techniques were used to study the sorption of p-xylene vapors on anhydrous and hydrated quartz sand in Chapter 3. The effect of salt treatments on vapor-phase sorption, and a comparison of batch and GC data are also presented. In addition, the advantages and limitations of GC methods for the study of vapor-phase sorption on soil materials are discussed.

Table 1-3. Selected physicochemical properties of p-xylene.

Property	Value[a]
Structure	$C_6H_4(CH_3)_2$
Molecular Weight	106.17 g/mole
Boiling Point	138.4°C
Density	0.86 g/mL (20°C)
Solubility	198 mg/L (25°C)
Vapor Pressure	8.14 mm Hg (24°C)
Henry's Law Constant	7.44 X 10^{-3} m^3· atm/mole

[a] Data obtained from Verschueren (1983) and Weast (1987).

In Chapter 4, the adsorption of p-xylene vapors on Ca-, Na-, and Li-saturated kaolin was measured using the flow-equilibration method. The effect of cation saturation on the competitive adsorption of water and p-xylene vapors was also studied. These data were used to evaluate the two-component BET adsorption models of Hill (1946a, 1946b) and Rhue et al. (1989).

Li-saturated kaolin was utilized as a reference surface for the study of water and organic vapor sorption in Chapter 4. However, there has been considerable debate in the literature as to whether or not Li-kaolin actually represents a surface free of cation hydration effects. Thus, the mechanism responsible for reduced water adsorption on Li-kaolin was investigated by gravimetric, spectroscopic, and ion extraction techniques in Chapter 5.

CHAPTER 2
VAPOR-PHASE SORPTION OF P-XYLENE AND WATER ON SOIL MATERIALS AT HIGH RELATIVE HUMIDITIES

Introduction

Vapor-phase sorption influences the mobility and distribution of volatile organic chemicals (VOCs) in the unsaturated zone as well as the atmospheric transport and deposition of VOCs. Previous studies have demonstrated that oven-dry soils and clay minerals have a sizable capacity to adsorb organic vapors, which can be described by the Brunauer-Emmett-Teller (BET) model (Call, 1957; Chiou and Shoup, 1985; Jurinak and Volman, 1957; Poe et al., 1988; Rao et al., 1989; Rhue et al., 1988). However, under natural conditions the sorption of organic vapors usually occurs on surfaces containing at least some adsorbed water. As the soil moisture content or relative humidity (RH) increases VOCs are displaced from the surface, resulting in the suppression of VOC sorption (Call, 1957; Chiou and Shoup, 1985; Hollist and Foy, 1971; Rao et al., 1989; Rhue et al., 1988, 1989; Spencer and Cliath, 1970, 1972, 1974, Wade, 1954). It is generally agreed that water effectively competes with organic vapors for mineral surfaces due to the polar nature of water and mineral adsorption sites (Valsaraj and Thibodeaux, 1988).

At RHs above which the sorbent surface is occupied by at least a monolayer of water, the specific mechanisms responsible for the sorption of VOCs

remain unclear. It has been postulated that the sorption of organic vapors at high RH can be described by partitioning into organic carbon (OC) (Chiou and Shoup, 1985). This hypothesis was based on the linear nature of benzene and chlorobenzene vapor sorption isotherms obtained for Woodburn soil (1.9% organic matter) at 90% RH, and the similarity between the magnitude of solute uptake from the aqueous and vapor phase (Chiou and Shoup, 1985). However, at 90% RH, Call (1957) obtained linear isotherms for the sorption of ethylene dibromide (EDB) vapors on Ca-saturated montmorillonite which contained no detectable OC. Rhue et al. (1989) also reported linear isotherms for p-xylene vapor sorption on sorbents with low OC contents; e.g., kaolin (0.65 g OC/kg) and silica gel (0.45 g OC/kg), at 67% relative humidity. In addition, sorption coefficients normalized for OC (K_{oc}) calculated from p-xylene sorption data and solubility considerations were 2 to 5 orders of magnitude greater than p-xylene K_{oc} values reported in the literature. A similar trend was noted by Peterson et al. (1988), who reported that linear sorption coefficients measured for trichloroethylene (TCE) vapor over a range of unsaturated conditions were 1 to 4 orders of magnitude greater than values obtained under saturated conditions. Chiou and Shoup (1985) also found that the vapor-phase sorption of benzene, m-dichlorobenzene, and 1,2,4-trichlorobenzene was consistently greater than sorption from aqueous solution, even though the sorbent surface should have been covered with several monolayers of water at 90% RH. These data suggest that in addition to partitioning into soil organic carbon, other mechanisms contribute to VOC sorption at high RH.

Dissolution into adsorbed water films and adsorption at the gas-liquid interface were considered by Call (1957) to be the dominant mechanisms responsible for EDB sorption on moist soils. For sparingly-soluble VOCs, such as p-xylene, the magnitude of sorption is far greater than dissolution into sorbed water, based on solubility limits in bulk water (Rhue et al., 1989). However, adsorption at the interface between the vapor phase and bulk water has been reported for a number of sparingly-soluble VOCs (Blank and Ottewill, 1964; Cutting and Jones, 1955; Drozd et al., 1982; Hauxwell and Ottewill, 1968). Due to the large surface area to volume ratio of adsorbed water films, adsorption at the gas-liquid interface of hydrated soils could contribute significantly to vapor-phase sorption.

The experiments reported here were designed to determine the nature of p-xylene vapor sorption isotherms at high RH and to determine the amount of p-xylene sorption attributable to adsorption at the gas-liquid interface, dissolution into adsorbed water films, and partitioning into OC. Adsorption at the gas-liquid interface was estimated from surface tension measurements of distilled water exposed to p-xylene vapors using the Gibbs adsorption equation.

Materials and Methods

Sorbents

The sorbents used in this study were selected to provide a range of surface area and OC content. Colloidal kaolin (K-6, Lot #731063) was obtained from

Fisher Scientific Products. The kaolin had a cation exchange capacity (CEC) of 4.23 $cmol_c/kg$ at pH 5.5 and was predominantly Na-saturated with only trace amounts of Ca, K, and Mg (Rhue et al., 1989). Silica gel (Syloid 244), average particle size of 3 μm and a pore volume of 1.4 cm^3/g, was obtained from the Davison Chemical Division, W.R. Grace & Co., Baltimore, MD. The Webster soil, a silty clay loam (Typic Haplaquoll), was collected from the surface horizon (0-30 cm) of a site in Iowa and ground to pass a 106 μm mesh screen. The Webster soil had a CEC of 51.11 $cmol_c/kg$ and was predominantly Ca-saturated. A portion of the Webster soil (Webster HP) was treated with hydrogen peroxide buffered to pH 5.0 with acetic acid to remove OC.

Organic carbon content was measured by the Wakley-Black heat-of-dilution method (Donohoe, 1983). The sorbent surface areas were determined from N_2 adsorption data (Advanced Materials Research Center, University of Florida). Cation exchange capacity was determined by washing the sorbents with 1.0 M $CaCl_2$ 5 times, removing excess salts with 95% ethanol until a negative chloride test was achieved using $AgNO_3$, and extracting exchangeable Ca with 0.5 M $Mg(NO_3)_2$. The amount of Ca present in the $Mg(NO_3)_2$ extract was then measured by atomic absorption spectroscopy. These and other sorbent properties are presented in Table 2-1.

Vapor-Phase Adsorption Studies

Vapor-phase sorption of p-xylene was determined on Webster soil and Webster HP at 0 and 90% RH, and on kaolin and silica gel at 0 and 67% RH. The

Table 2-1. Physical and chemical properties of sorbents used to study sorption of p-xylene vapors.

Sorbent	Organic Carbon	N_2 Surface Area	Cation Exchange Capacity	Particle Size Sand	Silt	Clay	Clay Mineralogy
	----g OC/kg----	--m^2/g--	----$cmol_c$/kg----	---------g/kg---------			
Kaolin[a]	0.65 (±0.02)	13.6	4.23 (±0.03)	0	150	850	kaolinite
Silica Gel[a]	0.45 (±0.08)	238.0	--------	------	------	------	amorphous
Webster Soil	41.36 (±0.23)	2.6	51.11 (±0.53)	550	200	250	smectite, kaolinite, mica
Webster HP	2.27 (±0.09)	33.0	31.89 (±0.12)	550	200	250	smectite, kaolinite, mica

[a] Adapted from Rhue et al. (1989).

flow-equilibration apparatus used to measure p-xylene and water vapor sorption was similar to that described in previous studies (Rhue et al., 1988, 1989). However, the p-xylene flow stream consisted of two gas washing bottles in series; the first contained water and the second contained p-xylene and water (Figure 2-1). This allowed the RH to be maintained at either 67 or 90% while the p-xylene relative vapor pressure (P/P_o) could be varied from 0 to 0.9, where P is the equilibrium vapor pressure and P_o is the saturated vapor pressure. The P_o of p-xylene at 24°C is 8.14 mm Hg, which is equivalent to a vapor concentration 46.64 mg/L (Weast, 1987). For sorption experiments conducted at 0% RH, valve V_3 was closed and valves V_1 and V_2 were adjusted to obtain relative vapor pressures of p-xylene ranging from 0 to 0.9.

The concentration of water and p-xylene vapor in the flow stream was determined by passing the flow stream through three polyethylene tubes in series. The three tubes contained magnesium perchlorate, activated charcoal, and a mixture of activated charcoal and magnesium perchlorate, respectively. The difference between the initial and final trap weights yielded the total mass of vapor trapped. The p-xylene vapor concentration was then determined by bubbling the flow stream through two 40-mL glass centrifuge tubes containing 20 mL of methanol. P-xylene trapped in these solutions was measured with a Perkin Elmer Model 320 UV-VIS spectrophotometer. The concentration of water vapor in the flow stream was determined by subtracting the concentration of p-xylene from the total vapor concentration.

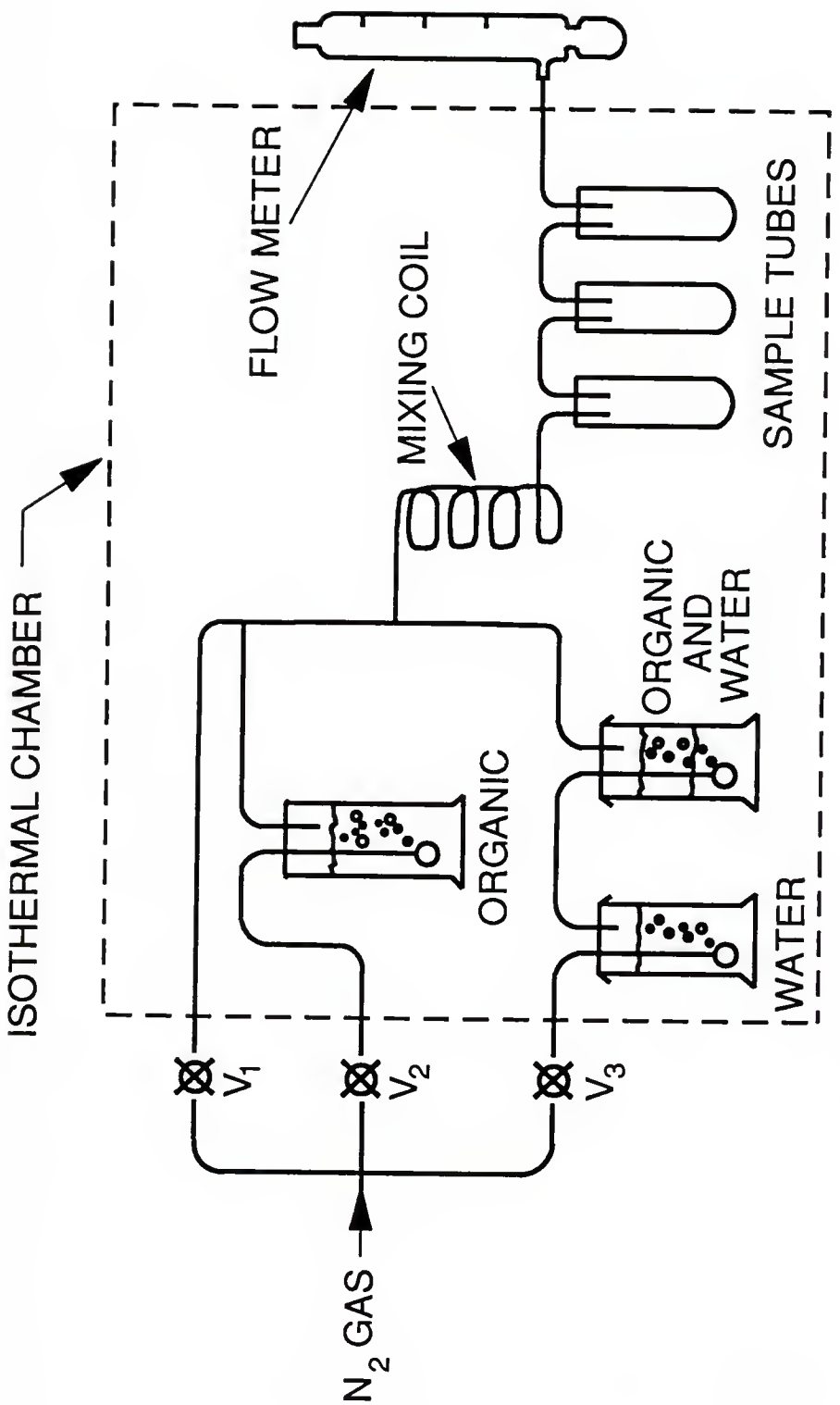

Figure 2-1. Flow-equilibration apparatus used to study sorption of p-xylene and water vapors on silica gel, kaolin, Webster soil, and Webster HP.

Approximately 1 g of sorbent, which had been oven-dried to 130°C, was placed in glass centrifuge tubes and capped with teflon-backed septa. Four tubes containing sorbent, and four blank tubes were placed on the flow stream in series. The gas flow stream passed through the centrifuge tubes via hypodermic needles at a rate of approximately 1.0 mL/sec. In general, an exposure time of 24 hours was sufficient to attain sorption equilibrium.

Adsorbed concentrations of water and p-xylene were measured by extracting the sorbents with 20 mL of methanol containing $CaCl_2$. The methanol solution was made by adding 10 mL of $CaCl_2$-saturated methanol per 1 L of methanol. Water in the methanol extract was measured by Karl Fisher (KF) titration. The KF reagent was diluted with KF diluent to a strength of approximately 0.5 mL titer per mg of water. The visual endpoint was established by adding titer to 20 mL of $CaCl_2$-methanol solution until the desired endpoint was obtained. In a second centrifuge tube, 5 mL of methanol solution was pretitrated to the visual endpoint and 10 μL of deionized water was injected and titrated to the endpoint to give the exact strength of the titer. A known volume of the methanol extract was titrated in a similar manner to determine the amount of adsorbed water.

The concentration of p-xylene in the methanol extract of kaolin and silica gel was measured using a Perkin Elmer Model 320 UV-VIS spectrophotometer. The Webster soil and Webster HP released methanol-soluble compounds that interfered with direct UV spectrophotometric analysis. Therefore, p-xylene extracts from these sorbents were analyzed by high-performance liquid chromatography

(HPLC) techniques. The HPLC system consisted of a Gilson 302 pump, Waters 450 detector, Hewlett Packard 3392A integrator, and a 10-cm Waters RCM C-18 column with a 3-cm Brownlee guard column.

Surface Tension Measurements

The surface tension of deionized water exposed to p-xylene vapors was measured using the "drop weight" method. The technique is based on Tate's law, which considers the weight of a drop falling from a small diameter tube to be proportional to the radius (r) of the tip (cm), and the surface tension (γ) of the liquid (g/s^2),

$$\text{weight per drop} = 2\,\pi\,r\,\gamma. \qquad (2\text{-}1)$$

Tate's law assumes that a spherical drop will form at the tip, but in reality the drop tends to elongate before it detaches from the tip. Harkins and Brown (1919) recognized the importance of this discrepancy and developed a correction factor (CF) based on the ratio of the tip radius to the length of the drop,

$$CF = f(r/V^{1/3}) \qquad (2\text{-}2)$$

where V is the volume of the drop (Table 2-2). In general, the values of $r/V^{1/3}$ were between 0.45 and 0.50. The following equation was then used to calculate surface tension:

$$\gamma = \frac{m\,g}{2\,\pi\,r\,CF}, \qquad (2\text{-}3)$$

where m is the mass of the drop (g), and g is the acceleration due to gravity (cm/s^2).

Table 2-2. Drop-weight surface tension correction factors (CF) adapted from Harkins and Brown (1919).

$r/V^{1/3}$	CF	$r/V^{1/3}$	CF
0.30	0.7256	0.75	0.6032
0.35	0.7011	0.80	0.6000
0.40	0.6828	0.85	0.5992
0.45	0.6669	0.90	0.5998
0.50	0.6515	0.95	0.6034
0.55	0.6362	1.00	0.6098
0.60	0.6250	1.05	0.6179
0.65	0.6171	1.10	0.6280
0.70	0.6093	1.15	0.6407

A 10-mL graduated burette was used for the surface tension measurements. After carefully grinding the tip flush, an ocular microscope was used to measure the diameter of the tip (0.37 cm). Drops of water falling from the tip were collected in a 40-mL centrifuge tube, capped with a teflon-backed septa. A 0.4-cm diameter hole was cut in the septa, and the height of the centrifuge tube was adjusted to achieve a tight seal between the septa and the burette. A total of 18-20 drops, at a rate of 4-6 drops per minute, were collected in the centrifuge tube. The surface tension of water was then calculated from the volume and weight of liquid collected. Solutions of NaCl were used to calibrate the diameter of the tip (0.3724 cm).

p-Xylene vapor, at relative vapor pressures from 0.1 to 0.8, was bubbled through a 50-mL centrifuge tube capped with teflon-backed septa. The tube contained approximately 40 mL of deionized water. No detectable change in the p-xylene concentration was measured after one, two or four days of bubbling. Therefore, the system was allowed to equilibrate for at least 24 hours. The surface tension of deionized water exposed to p-xylene vapors was determined in the same manner as described previously except that the p-xylene vapor was allowed to flow through the collection tube for at least 2 minutes prior to initiating the flow of drops.

Results and Discussion

Adsorption at 0% RH

Figures 2-2 and 2-3 show equilibrium isotherms for p-xylene vapor sorption on silica gel, kaolin, Webster soil, and Webster HP at 24°C. Sorption data are expressed as milligrams of p-xylene sorbed per gram of sorbent (S) versus the p-xylene relative vapor pressure (P/P_o). At 0% RH, the p-xylene isotherms of all four sorbents conformed to Type-II BET adsorption isotherms. This type of isotherm is typical of unrestricted monolayer-multilayer adsorption of gases on nonporous or macroporous (pore width > 0.05 μm) sorbents (Sing et al., 1985). These sorption data were fit by a least squares procedure to the linear form of the BET equation,

$$\frac{P/P_o}{S(1-P/P_o)} = \frac{1}{S_mC} + \frac{(C-1)P/P_o}{S_mC} \qquad (2\text{-}4)$$

where S_m is the nominal monolayer adsorption capacity (mg/g), and C is a parameter related to the heat of adsorption. Estimated values of S_m, C, and the P/P_o associated with monolayer coverage are presented in Table 2-3.

The BET equation is considered to give reliable estimates of S_m for surfaces exhibiting Type-II adsorption isotherms. However, the value of C does not provide a quantitative measure of the heat of adsorption, but does give an indication of the relative magnitude of sorbent-sorbate interactions (Sing et al., 1985). The values of C obtained for these systems are indicative of low sorbate-sorbent interactions associated with physical adsorption. For systems exhibiting low values of C,

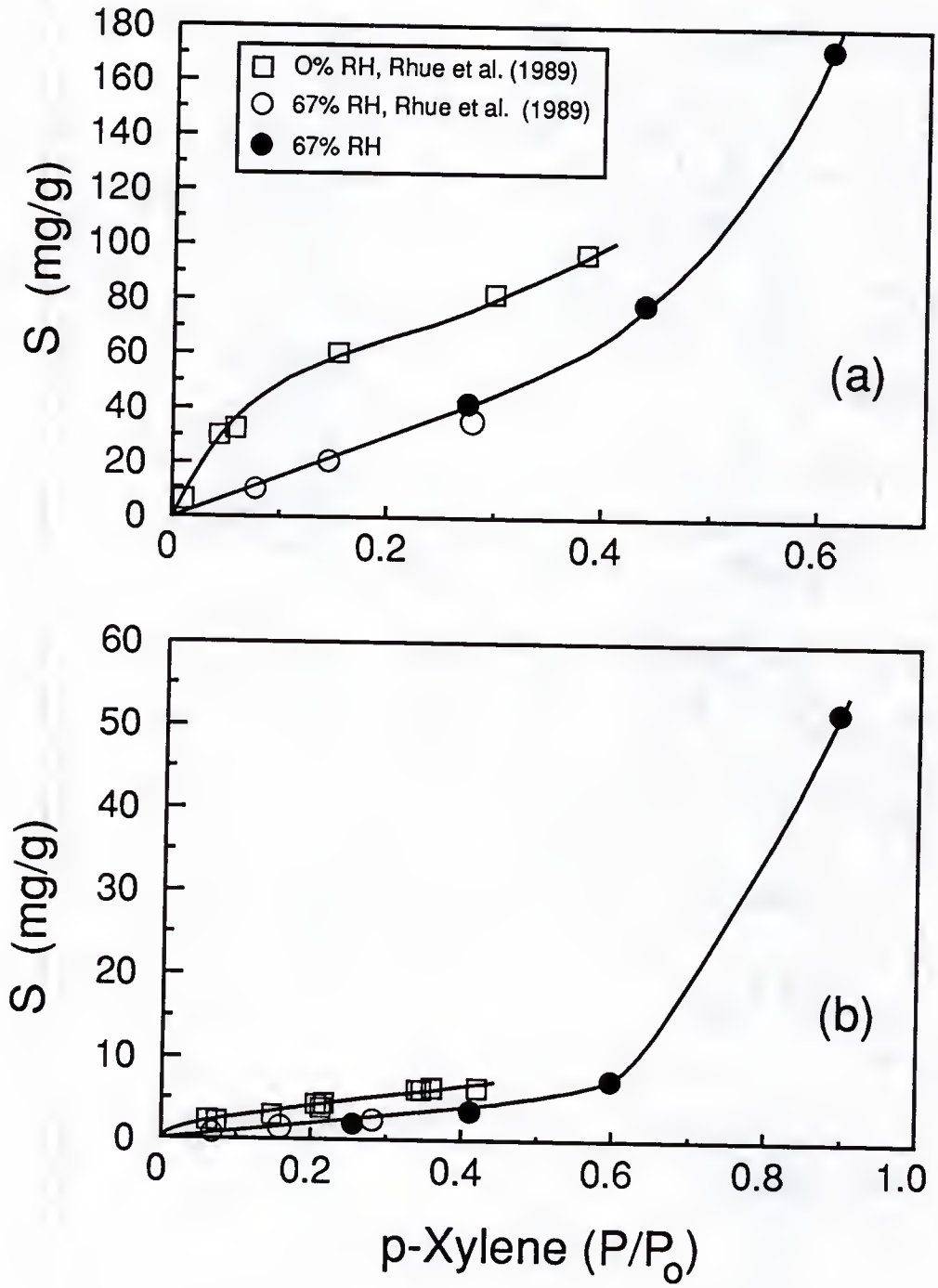

Figure 2-2. Sorption of p-xylene on (a) silica gel and (b) kaolin at 0 and 67% RH.

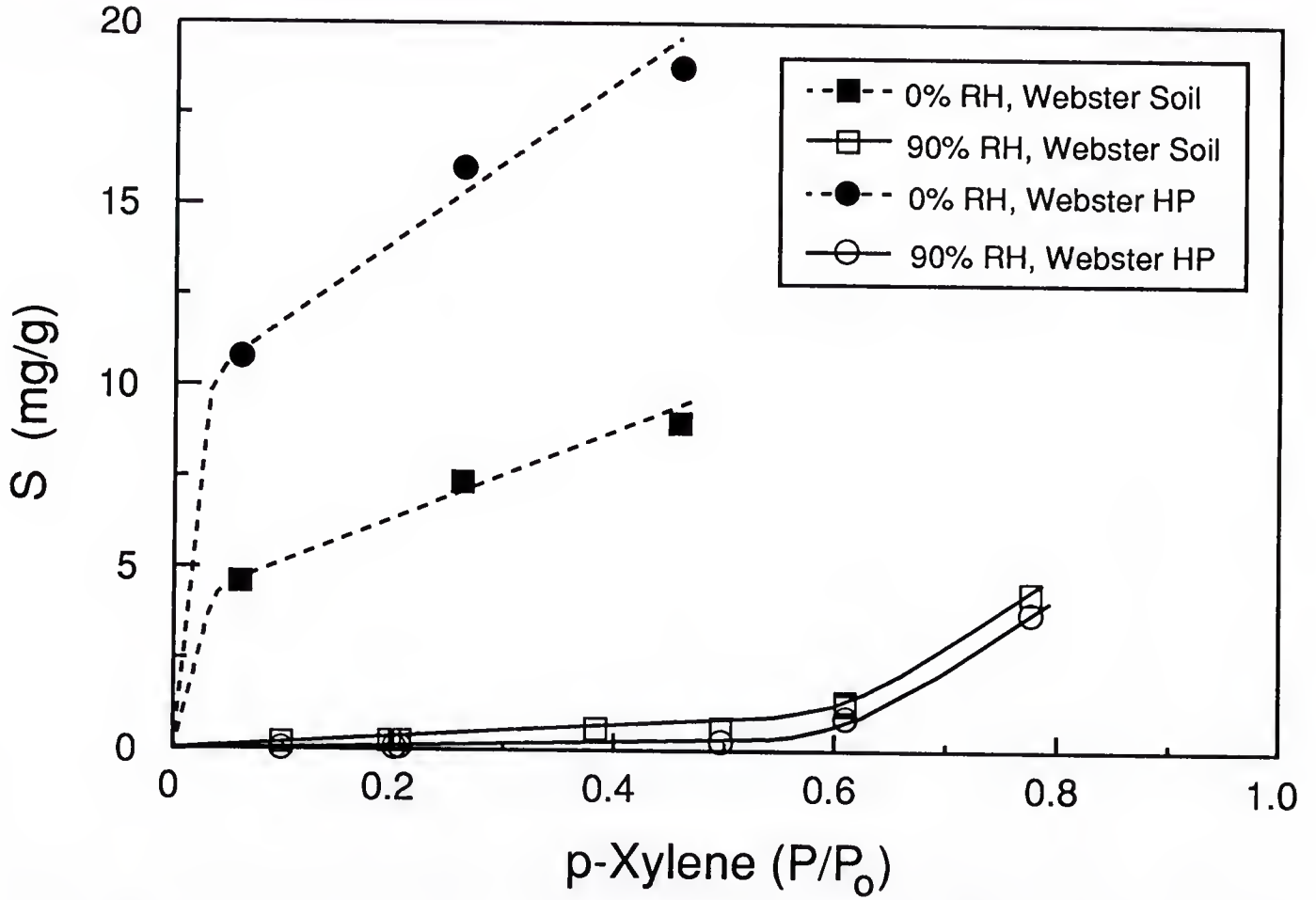

Figure 2-3. Sorption of p-xylene vapors on Webster soil and Webster HP at 0 and 90% RH.

Table 2-3. BET parameters calculated from single-sorbate adsorption isotherms.

Sorbent	Sorbate	S_m	C	BET Surface Area	P/P_o monolayer	P/P_o Range Used
Kaolin[a]	p-xylene	4.5	14	15	0.21	0.065-0.424
	water	4.2	20	10	0.18	0.056-0.481
Silica Gel[a]	p-xylene	64.7	17	139	0.20	0.003-0.387
	water	33.8	18	19	0.18	0.027-0.348
Webster Soil	p-xylene	5.7	48	12	0.13	0.061-0.264
Webster HP	p-xylene	12.3	73	27	0.10	0.061-0.262

[a] Adapted from Rhue et al. (1989).

discrete regions of multilayer sorption (i.e., patches) may form prior to the attainment of complete monolayer coverage (Jurinak and Volman, 1957; Sing et al., 1985).

The amount of sorbent surface available for the adsorption of a given molecule (S_{mA}) can be estimated from the S_m value and the area occupied by each adsorbed molecule. The cross-sectional areas (a_m) of water and p-xylene were calculated to be 0.105 and 0.380 nm^2, respectively, using the following equation (Karnaukhov, 1985; McClellan and Harnsberger, 1967),

$$a_m = 1.09(MW/\tau A)^{2/3} \qquad (2\text{-}5)$$

where MW is the molecular weight, τ is the liquid density, and A is Avogadro's number. This equation assumes that the sorbate molecules are oriented in a hexagonal close packing at a density similar to that of the bulk liquid. The surface areas occupied by either p-xylene or water molecules at monolayer coverage (S_{mA}) are shown in Table 2-3.

The values of S_{mA} for oven-dry kaolin and Webster HP were similar to those determined from N_2 adsorption isotherms. These data are consistent with the findings of Jurinak and Volman (1957) and Rhue et al. (1989), who concluded that the N_2 surface area provides a reasonable estimate of the area available for the sorption of organic vapors on predominantly mineral surfaces. It is interesting to note that the surface area of Webster soil, as determined from N_2 and p-xylene adsorption isotherms, increased following the hydrogen peroxide treatment. These data suggest that both p-xylene and N_2 vapors have a greater affinity for mineral

surfaces than for organic matter at 0% RH. The difference between the N_2 (2.62 m^2/g) and p-xylene/BET surface area (12 m^2/g) of Webster soil may have been due to greater sorption of p-xylene vapor by soil organic matter. This hypothesis is supported by the work of Chiou and Shoup (1985), who found that the adsorption of vapors on oven-dry Woodburn soil increased with the polarity of the sorbate. The discrepancy between the N_2 and BET surface area of silica gel has been discussed in a previous paper (Rhue et al., 1989)

The relative sorption (S/S_m) of p-xylene on oven-dry kaolin, silica gel, Webster soil, and Webster HP is shown in Figure 2-4. The use of S/S_m allows for the comparison of the adsorptive capacities of various sorbents on a unit-surface-area basis. At low values of P/P_o, the relative sorption of p-xylene on Webster HP and Webster soil was slightly greater than that on kaolin and silica gel. The increased sorption corresponds to an increase in the value of C for Webster soil (C = 38) and Webster HP (C = 73), which suggests that specific sorbate-sorbent interactions may have occurred. However, the overall similarity in relative sorption for the sorbents studied here suggests that the adsorption of p-xylene vapors at 0% RH was primarily a function of surface area.

Sorption at High RH

Vapor-phase sorption of p-xylene on silica gel and kaolin decreased dramatically when the RH was raised to 67% (Figure 2-2). The observed suppression of vapor-phase sorption at high RH is in agreement with the findings of others (e.g., Call, 1957; Chiou and Shoup, 1985; Rhue et al., 1989), and lends

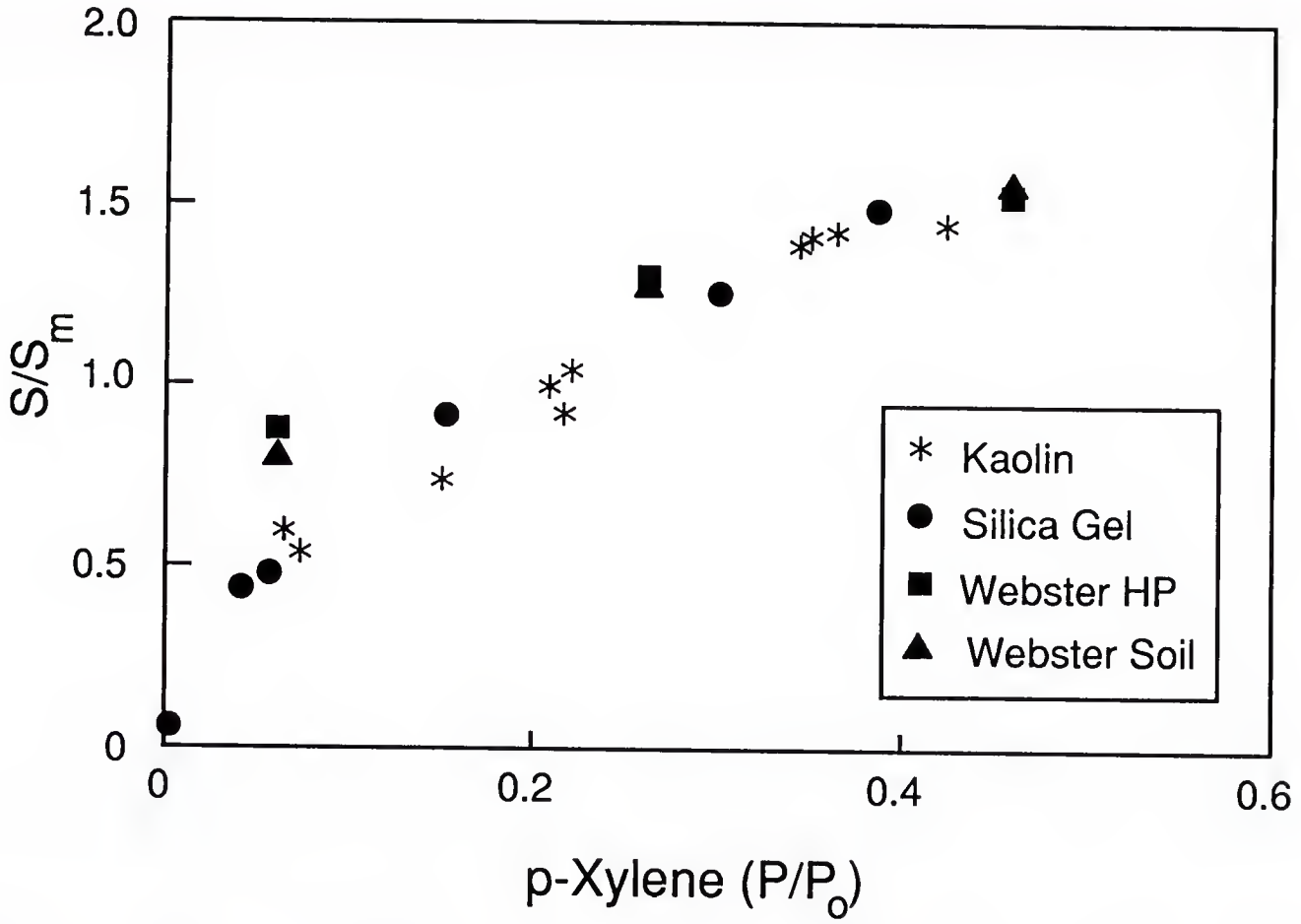

Figure 2-4. Sorption of p-xylene vapors normalized to values of S_m determined from the BET equation for silica gel, kaolin, Webster soil, and Webster HP at 0% RH.

further support to the contention that water effectively competes with organic vapors for mineral surfaces. Sorption of p-xylene vapors on Webster soil and Webster HP was also reduced at 90% RH (Figure 2-3). In addition, the sorptive capacity of Webster soil at 90% RH was greater than that of Webster HP, while the reverse was true at 0% RH. These data suggest that OC contributed to vapor sorption on Webster soil at high RH, while adsorption on mineral surfaces was the dominant mechanism at 0% RH.

At both 67 and 90% RH, p-xylene sorption isotherms were linear until the P/P_o reached approximately 0.5, above which, the amount of p-xylene sorbed increased sharply, resulting in Type-III adsorption isotherms. The linear nature of the sorption isotherms below 0.5 P/P_o was consistent with isotherms obtained by Call (1957) for EDB, and by Chiou and Shoup (1985) for benzene and chlorobenzenes. Increased sorption at high relative vapor pressures has not been previously reported for batch adsorption studies. However, researchers studying sorption of hydrocarbons on hydrated silica and soil materials by gas chromatography techniques have consistently obtained retention data which yield Type-III adsorption isotherms (Dorris and Gray, 1981; Karger et al., 1971a; Okamura and Sawyer, 1973). Therefore, hydrated soils appear to have a sizable capacity for organic vapor sorption when the relative vapor pressure approaches one.

The sorption of organic vapors at high RH is commonly described by dissolution of organic vapors into sorbed water films, using Henry's Law constants

(K_H), and subsequent solute partitioning into organic carbon, using sorption coefficients normalized for OC content (K_{oc}). The justification for such an approach comes primarily from a single article by Chiou and Shoup (1985). In this work, the authors conclude that solute partitioning into organic carbon is the dominant mechanism responsible for organic vapor sorption at high RH based primarily on two pieces of evidence; (1) the linearity of the sorption isotherms and, (2) the similarity in sorptive capacity from the aqueous and vapor phase. However, the data presented here demonstrate that below 0.5 P/P_o linear isotherms can be obtained for sorbents with OC contents ranging from trace levels to 41 g OC/kg. Thus, the mere existence of a linear isotherm was not sufficient evidence to conclude that partitioning into organic carbon had occurred. In addition, the dramatic increase in sorption above 0.5 P/P_o was not consistent with partitioning theory.

In order to compare sorption from the aqueous and vapor phase, K_{oc} values were estimated from measured p-xylene sorption data for P/P_o below 0.5 (linear portion of the isotherm) and the aqueous concentration of p-xylene determined using a K_H value of 7.44 X 10^{-3} m^3· atm/mole (Table 2-4). Predicted p-xylene K_{oc} values for silica gel, kaolin, and Webster HP were 4, 2, and 1 orders-of-magnitude greater, respectively, than K_{oc} values determined from column studies (105-176 mL/g) (Brusseau et al.; Gamerdinger et al., submitted for publication in Environmental Science and Technology) and estimated from a log octanol-water partition coefficient of 3.15 (573 mL/g) (Karickhoff, 1984). However, the predicted

Table 2-4. Sorption coefficients normalized for organic carbon content (K_{oc}) calculated from p-xylene sorption data for P/P° of 0.06 to 0.50.

Sorbent	RH	OC Content	K_{oc}	r^2
	---(%)---	---g/kg---	-----ml/g-----	
Silica Gel	67	0.45	2.35×10^6	0.936
Kaolin	67	0.65	9.10×10^4	0.989
Webster HP	90	2.27	1.53×10^3	0.967
Webster Soil	90	41.36	2.17×10^2	0.907

p-xylene K_{oc} for Webster soil was within the range of literature values. Thus, as the sorbent OC content increased, the predicted K_{oc} value approached those reported in the literature. These data suggest that the utility of K_{oc} values for predicting vapor sorption was limited to sorbents with relatively high OC contents, at relative vapor pressures less than 0.5.

Adsorption at the Gas-Liquid Interface

Adsorption at the gas-liquid interface was considered as a possible mechanism to account for the sorption p-xylene vapors on sorbents with low OC contents and at high relative vapor pressures. The adsorption of insoluble and sparingly soluble hydrocarbons on water surfaces has been estimated by measuring the change in surface tension with the partial pressure of the organic vapor (Baumer and Findenegg, 1982; Blank and Ottewill, 1964; Cutting and Jones, 1955; Hauxwell and Ottewill, 1968; Jho et al., 1978). This approach is based on the Gibbs adsorption equation,

$$\Gamma = - \frac{d\gamma}{d\mu} \qquad (2\text{-}6)$$

where Γ is the surface excess (mol/cm^2), γ is the surface tension, and μ is the chemical potential. If the vapor is assumed to obey the ideal gas law, equation (2-6) can be written as,

$$\Gamma = - \frac{P}{RT} \frac{d\gamma}{dP} \qquad (2\text{-}7)$$

where P is the partial pressure of the organic vapor, R is the gas constant, and T is the temperature. The surface tension of distilled water exposed to p-xylene

vapor, as determined by the drop-weight method, is shown in Figure 2-5a. These data were fit by a least squares regression procedure to yield a slope which could be then used to calculate the surface excess as a function of the partial pressure using equation (2-7) (Figure 2-5b). The Type-III adsorption isotherm generated from this procedure were typical of those obtained for other aromatic hydrocarbons and indicates that water acts as a low energy surface toward the nonpolar vapor (Cutting and Jones, 1955; Vidal-Madjar et al., 1976). The amount of p-xylene adsorbed at the gas-liquid interface was estimated from the surface excess and the N_2 surface area of each sorbent (Table 2-5). In addition, the mass of p-xylene partitioned into organic carbon was predicted using a K_{oc} of 200 mL/g and a K_H of 7.44 X 10^{-3} $m^3 \cdot$ atm/mole, and while mass of p-xylene dissolved in adsorbed water was predicted using the K_H value and the measured amount of water adsorbed. The sum of the estimated values for these adsorption components represents the total predicted adsorption, which is compared to the measured adsorption data in Table 2-5. Adsorption on mineral surfaces was not included in the predicted total because water is generally assumed to displace organic vapors from mineral surfaces at high RH. However, the appropriateness of this assumption at 67% RH is discussed.

The predicted data indicated that the gas-liquid interface was the dominant mechanism responsible for vapor sorption on silica gel and kaolin. Neither partitioning into organic carbon nor dissolution into sorbed water contributed significantly to p-xylene sorption, due to the low OC content of these sorbents and

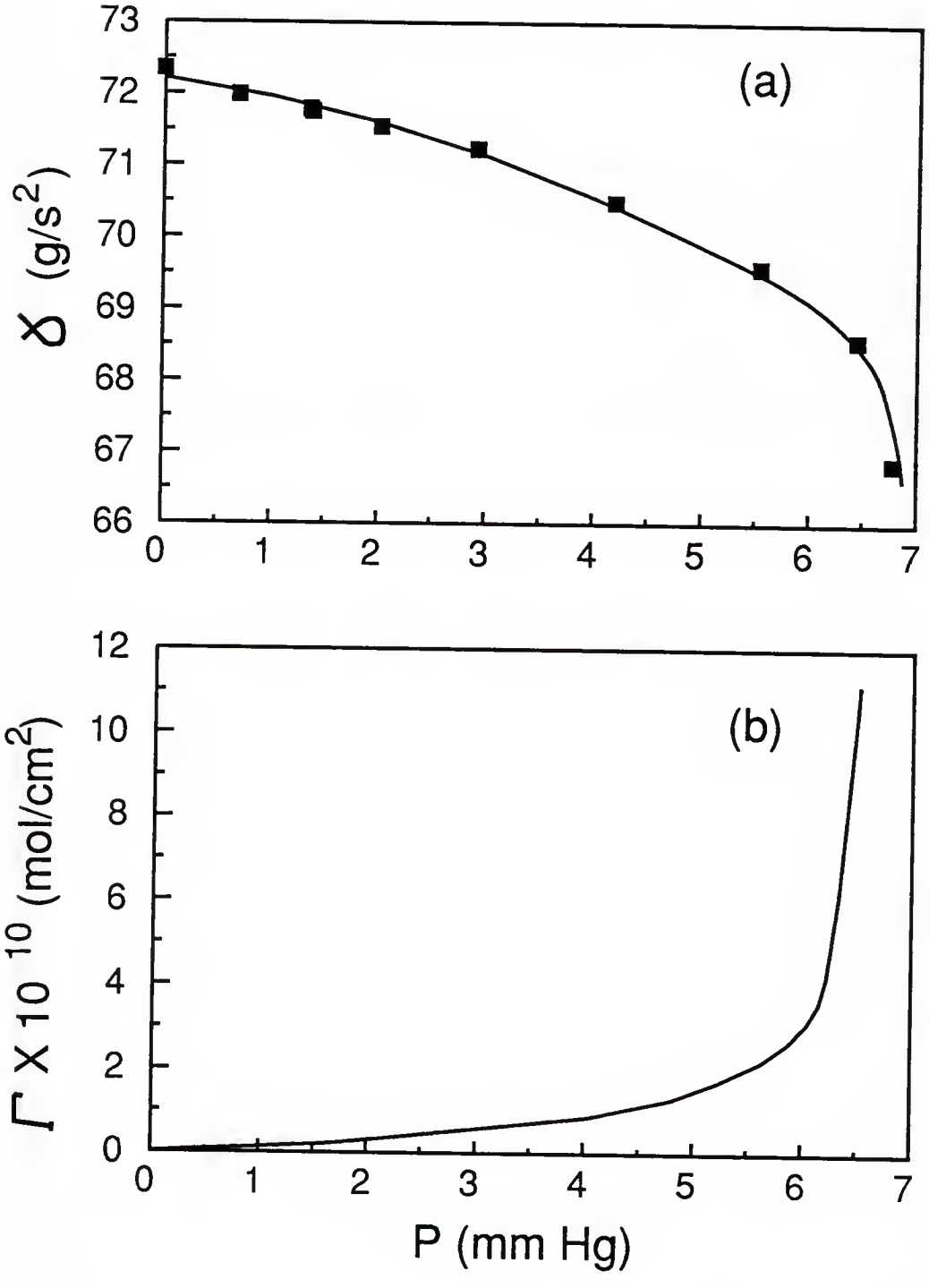

Figure 2-5. Surface tension (a) of deionized water exposed to p-xylene vapors at 24°C and surface excess (b) of p-xylene at the gas-liquid interface calculated using the Gibbs adsorption equation.

Table 2-5. Predicted and measured p-xylene sorption on Silica Gel, Kaolin, Webster HP, and Webster Soil at 90% RH.

Sorbent	P/P_o	Sorption by Components			Total Sorption	
		Gas-Liquid Interface	Organic Carbon	Sorbed Water	Predicted	Measured
		mg/g				
Silica Gel	0.081	1.802	0.001	0.001	1.804	11.61
	0.145	3.921	0.002	0.001	3.924	20.74
	0.274	10.052	0.004	0.002	10.058	41.95
	0.282	10.514	0.004	0.003	10.521	36.73
	0.439	21.522	0.006	0.004	21.532	80.19
	0.610	37.706	0.004	0.008	37.718	173.97
Kaolin	0.069	0.084	0.001	0.000	0.085	0.45
	0.164	0.267	0.003	0.000	0.270	1.41
	0.258	0.523	0.005	0.000	0.528	2.28
	0.286	0.614	0.006	0.000	0.620	2.77
	0.415	1.120	0.008	0.001	1.129	3.76
	0.600	2.094	0.012	0.001	2.107	7.71
	0.896	18.262	0.018	0.001	18.281	52.19
Webster HP	0.099	0.324	0.007	0.001	0.332	0.05
	0.201	0.870	0.014	0.003	0.887	0.08
	0.206	0.903	0.014	0.003	0.920	0.10
	0.497	3.677	0.034	0.007	3.718	0.28
	0.601	5.228	0.043	0.008	5.279	0.91
	0.777	14.014	0.054	0.009	14.077	3.88
Webster Soil	0.099	0.026	0.126	0.002	0.154	0.21
	0.197	0.067	0.251	0.003	0.321	0.26
	0.206	0.072	0.262	0.003	0.337	0.25
	0.384	0.190	0.488	0.005	0.683	0.61
	0.497	0.292	0.632	0.008	0.932	0.63
	0.610	0.415	0.776	0.008	1.199	1.31
	0.777	1.113	0.988	0.010	2.111	4.36

the low solubility of p-xylene, respectively. However, the total predicted sorption of p-xylene on silica gel and kaolin was approximately one-quarter of the measured amount. This discrepancy may have been due to adsorption of p-xylene vapors on exposed mineral surfaces. The average amount of water adsorbed on silica gel and kaolin at 67% RH was 57.9 and 9.3 mg/g, respectively, which is equivalent to 1.7 and 2.2 monolayers of water, based on BET estimates of S_m (Table 2-3). Due to the low values of C (20 and 18) for these sorbents, it was possible that patches of water formed on the mineral surface (Jurinak and Volman, 1957; Sing et al., 1985), thereby allowing for adsorption on exposed mineral surfaces. Even if monolayer coverage of water was attained, the mineral surface could still have exerted a surface effect on sorbed water films (Fowkes, 1968), resulting in greater sorption than would be predicted for bulk water surfaces. These hypotheses are supported by the work of Dorris and Gray (1981), who reported that the sorption coefficient for n-heptane on water-coated silica increased significantly at water contents less than those achieved at 88% RH. Therefore, it is quite possible that additional adsorption of p-xylene vapors occurred on exposed mineral surfaces and/or surface-affected water films of silica gel and kaolin.

Predicted p-xylene sorption on Webster HP was considerably greater than that measured with the flow-equilibration apparatus. Dissolution into sorbed water films and partitioning into organic carbon contributed very little to the overall estimate of p-xylene sorption on Webster HP. Thus, the difference between predicted and measured sorption was primarily the result of the estimate of

adsorption at the gas-liquid interface. The surface area would have to be reduced from 33.8 m^2/g to approximately 4 m^2/g in order to bring the estimated adsorption at the gas-liquid interface into agreement with the measured sorption data. In contrast, the predicted sorption of p-xylene on Webster soil was similar to the measured values. Partitioning of p-xylene into OC on Webster soil (41 g OC/kg) accounted for the majority of sorption at relative vapor pressures less that 0.6. Sorption at the gas-liquid interface of Webster soil was much less than that of Webster HP because the N_2 surface area was only 2.62 m^2/g.

Summary

The transport of VOCs in the unsaturated zone is directly influenced by partitioning of the organic chemical between the liquid, vapor, and solid phase. Of particular concern is the vapor phase, in which VOC transport may occur at a rate greater than that in the liquid phases. Thus, it is imperative that the mechanisms responsible for vapor-phase sorption are correctly identified and incorporated into VOC models.

For all sorbents studied here, vapor-phase sorption of p-xylene increased dramatically at relative vapor pressures greater than 0.5, resulting in Type-III adsorption isotherms. Although it is generally accepted that oven-dry sorbents have sizable sorption capacity for organic vapors, these data suggest that hydrated soil materials can also sorb significant quantities of organic vapors in regions of high vapor concentration (e.g., near the contaminant source). In addition, the data

presented here indicate that the use of K_{oc} values to predict vapor-phase sorption at high RH appears to be only valid for sorbents with high OC content, at relative vapor pressures less than 0.5. These findings are particularly important in light of the fact that most VOC and multi-phase transport models either fail to consider vapor-phase sorption (Pinder and Abriola, 1986; Sleep and Sykes, 1989) or describe vapor-phase sorption by dissolution into soil water and partitioning into OC (Baehr, 1987; Jury et al., 1990).

In order to describe vapor-phase sorption for different sorbate-sorbent systems over a range of relative vapor pressures, one must consider all mechanisms which contribute to VOC sorption. The data presented here indicate that a multi-mechanistic approach should include adsorption on mineral surfaces, partitioning into OC, dissolution into sorbed water films, and adsorption at the gas-liquid interface. Surface tension data suggest that adsorption at the gas-liquid interface could contribute significantly to the sorption of sparingly-soluble VOCs in the unsaturated zone. Of particular interest is the sizable surface excess estimated for aromatic hydrocarbons of environmental concern such as toluene, benzene, and o-xylene (Blank and Ottewill, 1964; Cutting and Jones, 1955; Hauxwell and Ottewill, 1968; Vidal-Madjar et al., 1976). The task at hand now is to further define the limits of applicability of each mechanism based on sorbate, sorbent, and environmental considerations, and to incorporate this knowledge into current modeling efforts. An initial attempt at this approach has been attempted by Shoemaker et al. (1990), who described vapor-phase sorption of TCE using an

"effective sorption" term that included sorption coefficients for the solid-liquid and the solid-gas interface.

CHAPTER 3
GAS CHROMATOGRAPHIC STUDIES OF P-XYLENE SORPTION ON ANHYDROUS AND HYDRATED QUARTZ SAND

Introduction

Gas-liquid chromatography (GLC) is recognized as an efficient and versatile method for investigating the sorption of volatile organic compounds (VOCs) on hydrated sorbents. The interpretation of GLC data requires a consideration of several retention mechanisms including (1) adsorption at the gas-liquid interface, (2) adsorption at the solid-liquid interface, and (3) partitioning into the liquid phase. Conder et al. (1969) proposed the following equation to describe the net retention volume (V_N) of a solute at infinite dilution:

$$V_N = K_L V_L + K_I A_I + K_S A_S \qquad (3\text{-}1)$$

where K_L (mL/mL), K_I (mL/m^2), and K_S (mL/m^2) are the distribution coefficients for the liquid phase, gas-liquid interface, and solid-liquid interface, respectively, V_L (mL/g) is the volume of the liquid phase, and A_I (m^2/g) and A_S (m^2/g) are the areas of the gas-liquid interface and solid-liquid interface, respectively. Previous studies have demonstrated that aliphatic hydrocarbon retention on water-coated supports is due solely to adsorption at the gas-liquid interface; whereas, aromatic hydrocarbons and other weakly polar solutes are simultaneously adsorbed at the gas-liquid interface and partitioned into the liquid phase (Karger et al., 1971a,

1971b; Martin, 1961). At water contents above 3 to 4% by weight, the effect of the solid support on solute retention appears to vanish, and thus equation (3-1) can be applied without the K_SA_S term (Dorris and Gray, 1981; Okamura and Sawyer, 1973). Comparisons of partition coefficients and heats of solution determined by GLC and static methods indicate that adsorbed water films between 1.5 and 200 nm in thickness have properties similar to those of bulk water (Karger et al., 1971a, 1971b; Chatterjee et al., 1973). Thus, gas chromatography (GC) appears to be an ideal method to study vapor-sorption at the gas-liquid interface, and can be utilized to measure sorption on anhydrous soil materials. A detailed review of the theoretical and experimental application of GC methods to the study of VOC sorption has been presented by Rhue and Rao (1990).

The adsorption of insoluble and sparingly-soluble hydrocarbons on water surfaces has also been estimated from measurements of the change in surface tension of bulk water with the partial pressure of the vapor, using the Gibbs adsorption equation. The surface excess of organic vapors calculated in this manner typically yields Type-III adsorption isotherms. In addition, heats of adsorption for n-hexane and toluene on bulk water were found to be greater than corresponding heats of vaporization (Hauxwell and Ottewill, 1968). Adamson (1967) attributed this behavior to the rearrangement of surface water molecules to accommodate the hydrocarbon, which resulted in larger heats of adsorption. Although measurements of vapor adsorption on water-coated supports by GLC yield Type-III adsorption isotherms (Dorris and Gray, 1981; Karger et al., 1971b;

King et al., 1972), heats of adsorption estimated from GLC data are generally smaller than heats of vaporization. These findings suggest that the gas-liquid interface of water acts as a low energy surface toward nonpolar vapors (Chatterjee et al., 1972; Dorris and Gray, 1981; Hartkopf and Karger, 1973; Karger et al., 1971a, 1971b). The discrepancy between heats of adsorption obtained from GLC and surface tension data has been attributed to uncertainty in surface tension measurements at low surface coverages (Dorris and Gray, 1981; Karger et al., 1971a, 1971b); whereas, flame-ionization detectors (FID) used in GLC studies provide accurate measurements of hydrocarbon adsorption.

In addition to high sensitivity, gas chromatography allows for the rapid collection of sorption data over a range of temperature and moisture content regimes. Despite the apparent advantages of GC techniques over conventional batch adsorption methods, relatively few studies have been conducted using soil material as the solid support phase (Bohn et al., 1980; Okamura and Sawyer, 1973; Rao et al., 1988). Thus, the purpose of this work was to test the utility of gas chromatography for the study of p-xylene sorption on anhydrous and hydrated quartz sand. The effect of $CaCl_2$ treatments on p-xylene adsorption was also investigated by GC, and was compared to adsorption data obtained by flow-equilibration and surface tension methods.

Materials and Methods

Column Preparation

The solid support material was collected from the B_h horizon of an Oldsmar soil (Alfic Arenic Haplaquod) located in Collier County, Florida. Mechanical analysis indicated that the sand-size fraction (diameter > 50 μm) accounted 90% of the soil sample. The Oldsmar soil sample had a cation exchange capacity of 5.2 $cmol_c/kg$ and was predominantly Ca-saturated. The N_2 surface area was 10.05 m^2/g, while the organic carbon content was 10.9 g OC/kg (Rhue et al., 1988). The soil sample used in the GC experiments was sieved to pass a 250 μm screen and will be referred to as Oldsmar sand. A portion of this sample was washed 3 times with 0.1 M $CaCl_2$ to test the effect of salt on vapor-phase sorption.

The Oldsmar sand was packed in 6.35 mm o.d. glass columns, approximately 16 and 90 cm in length. The 90-cm columns were used to measure sorption on hydrated sorbents; the additional length was necessary to obtain adequate solute separation. These columns were crafted to form a U-shape which matched the inlet and outlet ports of the gas chromatograph. As sand was added to the column, the column was gently vibrated to achieve uniform packing. Glass wool was placed at the ends of the columns to maintain support integrity.

Gas Chromatography Experiments

A Tracor 222 gas chromatograph equipped with a FID was used for the sorption studies. Certified grade p-xylene (99.8% purity) and high purity grade methane (99.97% purity) were obtained from Fisher Scientific Products. The FID was calibrated for p-xylene at three N_2 flow rates, with air and hydrogen flow rates

maintained at 0.65 mL/sec and 5.0 mL/sec, respectively. During calibration the p-xylene vapor was introduced onto a straight glass column by passing the N_2 flow stream over a thermostated sample of liquid p-xylene. When a constant mV reading was obtained, the flow stream was bubbled through a 40-mL centrifuge tube containing 20 mL of methanol. The concentration of p-xylene in the methanol was measured by UV-VIS spectroscopy or HPLC techniques.

The adsorption of p-xylene on untreated and salt-treated Oldsmar sand was measured under anhydrous and hydrated conditions at room temperature ($\approx$ 24°C). For anhydrous experiments, the column was allowed to equilibrate with "dry" N_2 for several hours prior to the initiation of p-xylene injections. This was analogous to the flow-equilibration method in which "dry" N_2 was used as the carrier gas. For hydrated systems, Okamura and Sawyer (1971, 1973) recommend that the desired water content be reached by desorption of a saturated column in order to attain uniform water coverages. However, this procedure resulted in the introduction of excessive quantities of water into the FID and associated column fittings. Dorris and Gray (1981) obtained reproducible solute retention data at water contents of 0.6, 1.4, and 3.8% by equilibrating the column with carrier gas at 26, 62, and 88% RH. For the experiments described here, relative humidities of 90 and 98% were achieved by bubbling the N_2 flow stream through a gas-washing bottle containing deionized water in a manner similar to that described in Chapter 2. The relative humidity of the N_2 flow stream was measured at the column inlet and outlet by trapping the water vapor in two magnesium perchlorate traps arranged in series.

In addition, the back pressure at the column inlet was measured using a pressure transducer, for which the mV output had been calibrated against pressure heads.

Adsorption isotherms for p-xylene were obtained by the eluted-pulse method of Dorris and Gray (1981). The retention time of methane (t_o) and p-xylene (t_r) vapors, which were simultaneously injected on the column, was recorded with a Hewlett Packard 3390A integrator. The retention time of air injections, which gave a negative response, were identical to those of methane. These data indicate that methane was not retained by the stationary phase. Thus, the net retention volume (V_N) of p-xylene was calculated from the difference between t_r and t_o, using the N_2 flow rate. Injections volumes ranging from 1 µL to 2 mL of p-xylene vapor were used to obtain a range of net retention volumes.

If the adsorption of p-xylene is assumed to occur on mineral surfaces for anhydrous sorbents, and solely by adsorption at the gas-liquid interface of water-coated supports, the net retention volume (V_N) required to elute a solute is given by,

$$V_N = RT(d\Gamma/dP)A = RT(dS/dP)w \qquad (3\text{-}2)$$

where R is the gas constant, T is the temperature, Γ is the surface concentration (mol/cm^2), P is the partial pressure of the vapor, A is the surface area, S is the amount adsorbed (mg/g), and w is the weight of the column packing (Dorris and Gray, 1981). Adsorption isotherms can then be obtained by integrating equation (3-2) as follows:

$$S = 1/RTw \int V_N(P)\, dP. \qquad (3\text{-}3)$$

The peak-maxima method of Dorris and Gray (1981) was employed to obtain a

chromatographic envelope which could be integrated by equation (3-3). The calibration curve described previously was used to convert mV readings, obtained from peak height measurements, to partial pressures of p-xylene. However, the use of equation (3-2) implies that the sorption effect and pressure gradient along the column were negligible.

Results and Discussion

Adsorption on Anhydrous Oldsmar Sand

Chromatographic peak maxima obtained from injections of p-xylene vapors on untreated and salt-treated Oldsmar sand are presented in Figure 3-1. Net retention volumes of p-xylene on untreated Oldsmar sand were larger than those of salt-treated soil, indicating greater solute retention. Adsorption in the Henry's Law region, characterized by highly symmetric peaks and net retention volumes independent of sample size, was not attained for untreated Oldsmar sand, even at p-xylene partial pressures of 2.5×10^{-3} mm Hg. In contrast, the salt-treated Oldsmar sand exhibited Henry's region adsorption at a net retention volume of approximately 5.2 mL. As greater quantities of p-xylene were injected, the net retention volume decreased until the peaks became asymmetric, at which point the net retention volume began to increase. Although not shown here, the position of the leading edge of the asymmetric peaks was similar, indicating that adsorption equilibrium was attained (Dorris and Gray, 1981). The connection of peak maxima

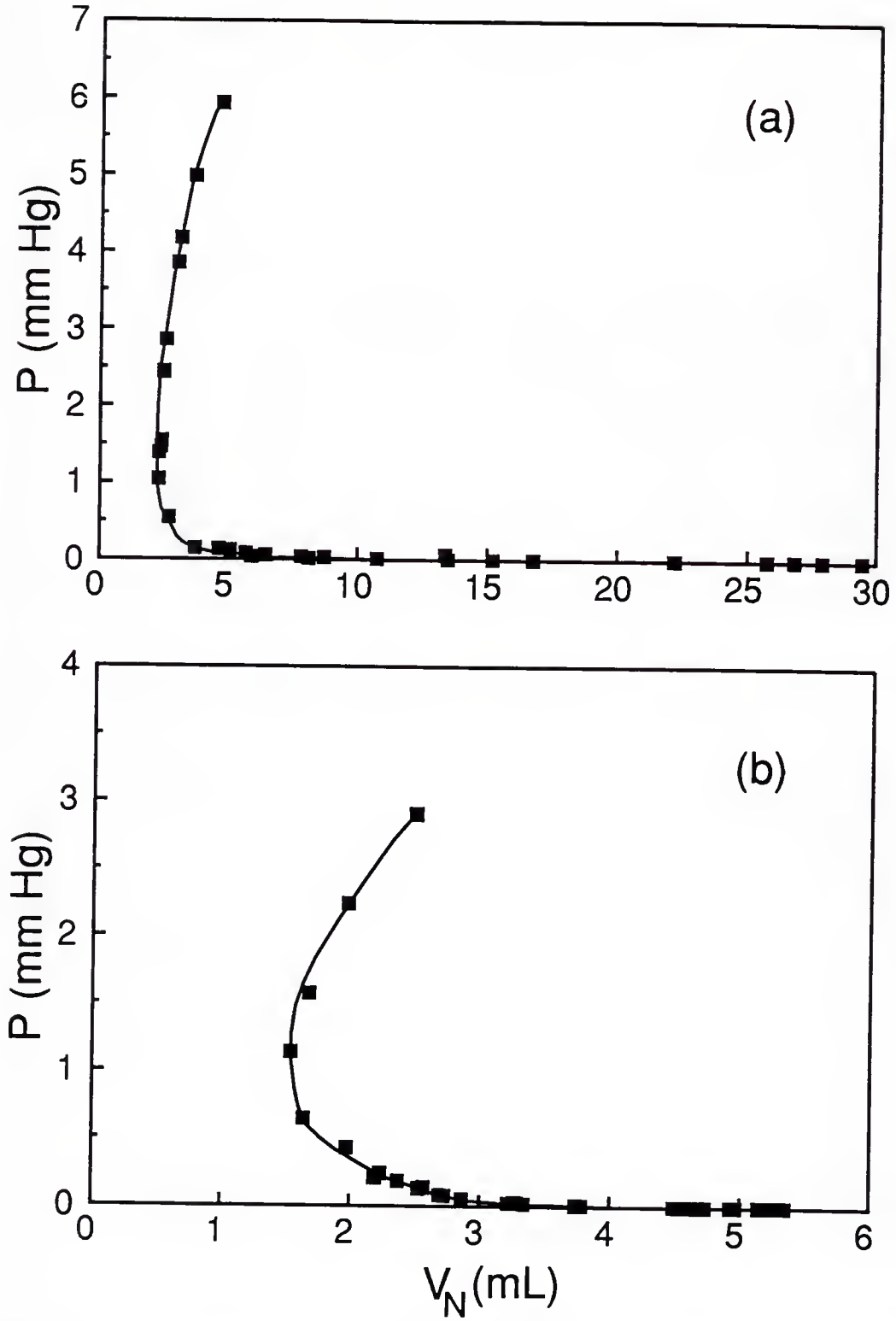

Figure 3-1. Chromatographic peak maxima at room temperature (≈24°C) for p-xylene vapor on (a) untreated Oldsmar soil and (b) salt-treated Oldsmar soil.

formed a chromatographic envelope which was integrated by equation (3-3). The resulting p-xylene adsorption isotherms are presented in Figure 3-2.

The adsorption of p-xylene on untreated Oldsmar sand yielded a Type-II isotherm, indicative of multilayer formation. A similar isotherm was obtained for the salt-treated sand, although the adsorption capacity was reduced. These data have yet to be confirmed by batch techniques; however, p-xylene adsorption on 250-425 μm Oldsmar sand measured by the GC and flow-equilibration methods were in close agreement (R. D. Rhue, 1990, personal communication).

The effect of the salt treatments on p-xylene adsorption by Webster soil was also studied using the flow equilibration apparatus described in Chapter 2 (Figure 3-3). Webster soil and Webster soil treated with hydrogen peroxide (Webster HP) was extracted with methanol containing $CaCl_2$ to measure water and p-xylene sorption. Following methanol extraction, the Webster soil and Webster HP contained 12.01 (±0.65) and 15.18 (±0.44) mg $CaCl_2$/g, respectively. Subsequent adsorption experiments indicated that in the presence of salt p-xylene vapor adsorption was reduced by 6.95 and 5.98 mg/g on Webster HP and Webster soil, respectively. These data were in aggreement with the observed decrease in the adsorptive capacity of Oldsmar sand following a salt treatment, measured by the eluted-pulse method. From a mechanistic perspective, the salt may have coated the adsorbent surface or reduced the surface charge, such that the magnitude of adsorbate-adsorbent interactions was decreased.

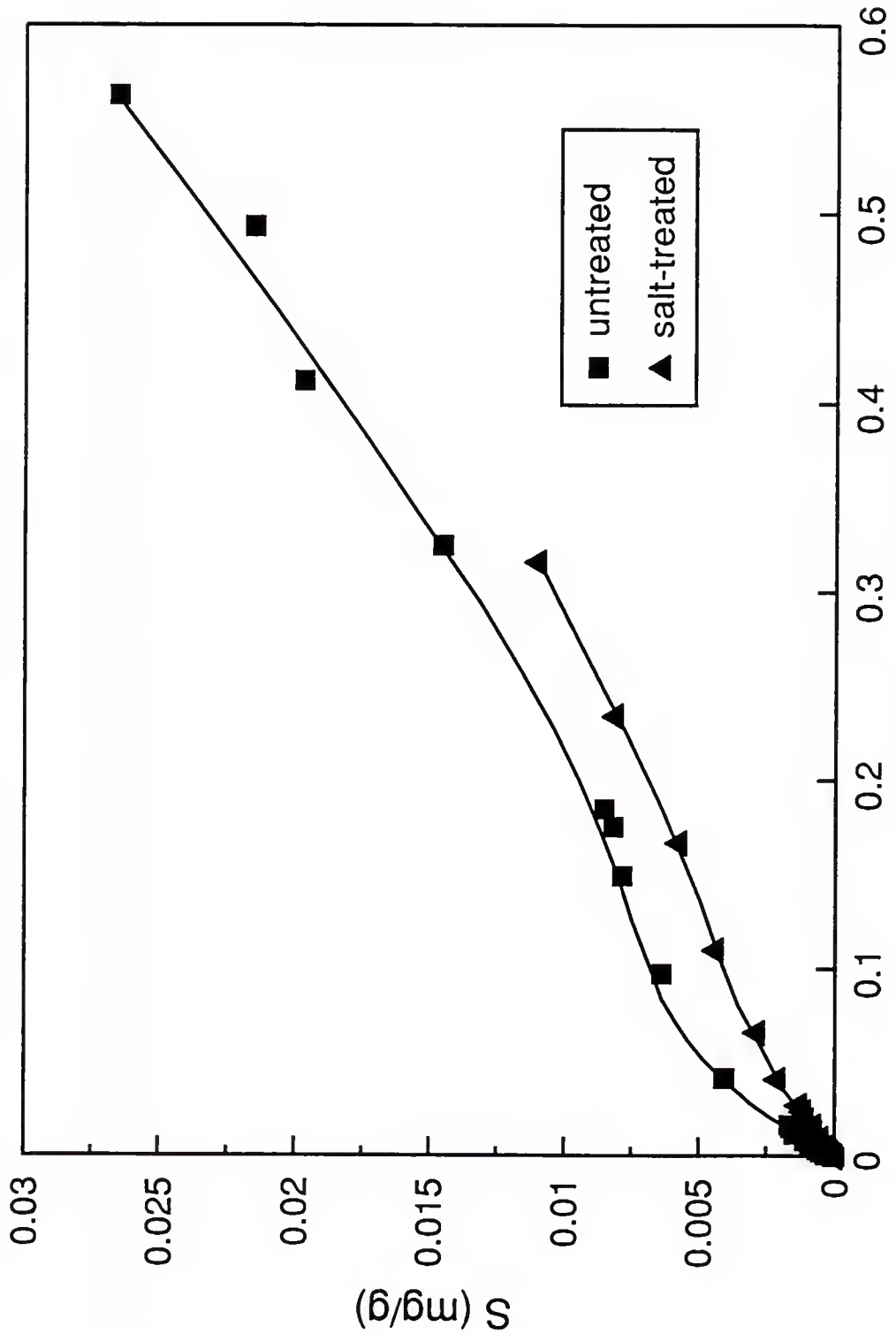

Figure 3-2. Adsorption isotherms for p-xylene vapor on untreated and salt-treated Oldsmar soil.

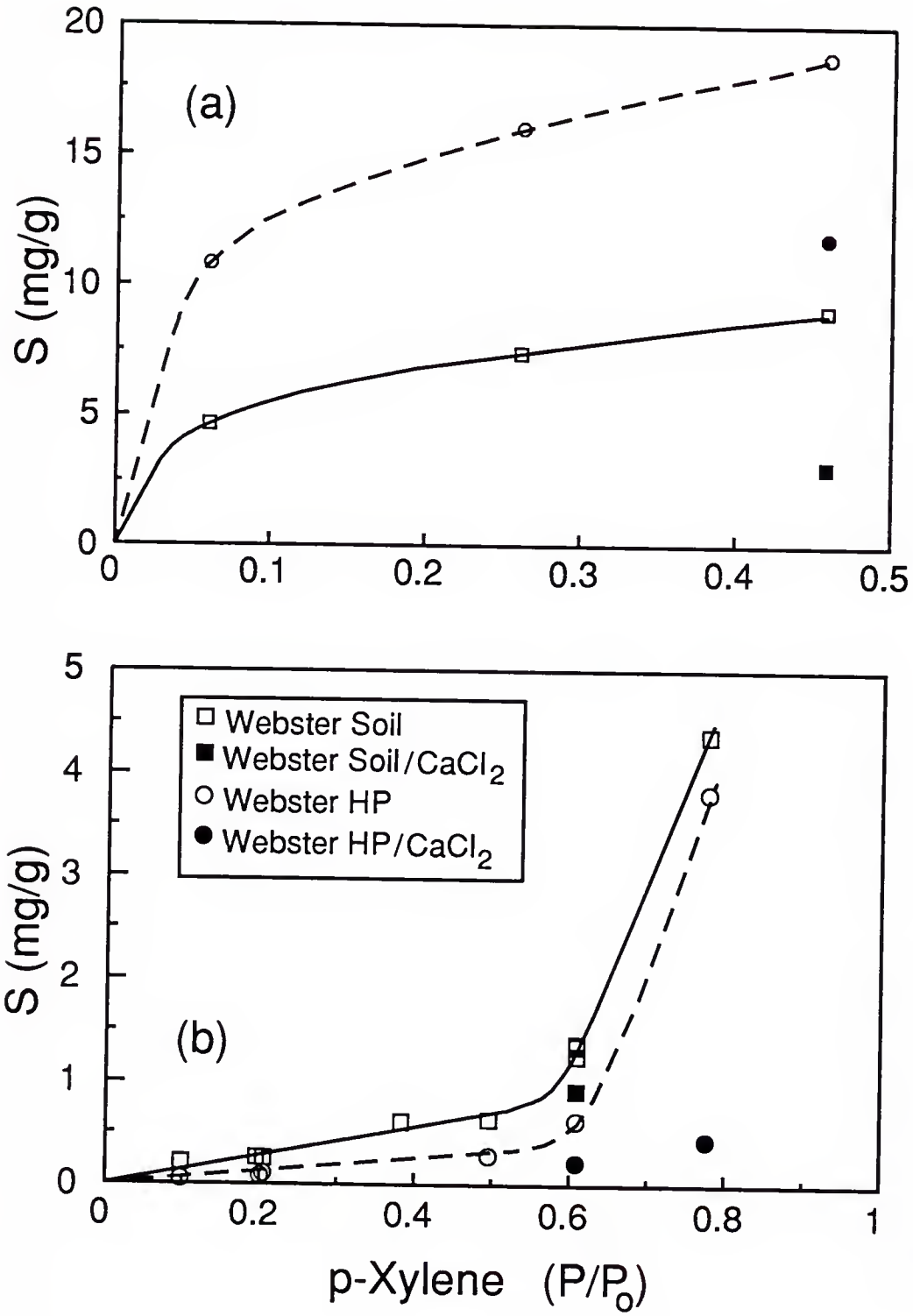

Figure 3-3. Adsorption of p-xylene vapors on Webster soil and Webster HP at (a) 0% RH and (b) 90% RH.

Adsorption on Hydrated Oldsmar Sand

The net retention volume of p-xylene injected onto 90-cm columns packed with Oldsmar sand decreased from approximately 297 mL to less than 8 mL when the RH was increased to 90%. This reduction was indicative of the effect of water on the retention of p-xylene vapors. Net retention volumes of p-xylene on salt-treated Oldsmar sand at 90% RH, and on untreated Oldsmar sand at 90 and 98% RH are presented in Figure 3-4. Henry's region adsorption occurred at smaller retention volumes, and for greater p-xylene partial pressures, than under anhydrous conditions. In addition, the value of V_N increased continuously, except in the Henry's Law region, which is characteristic of adsorption yielding Type-III isotherms (Dorris and Gray, 1981). At N_2 flow rates of 0.42 and 0.33 mL/s, the p-xylene net retention volumes were similar, demonstrating the internal consistency of the eluted-pulse method. Adsorption isotherms obtained from chromatographic envelopes of these data are presented in Figure 3-5.

The presence of water not only precipitated a shift from Type-II to Type-III adsorption isotherms, but also resulted in a substantial reduction in p-xylene adsorption. These findings are consistent with data reported in Chapter 2 for p-xylene sorption on silica gel and kaolin at 67% RH, and on Webster soil and Webster HP at 90% RH. At 98% RH an additional reduction in p-xylene adsorption on Oldsmar sand was observed. These data suggest that sorbent surface was not completely covered with water or that the surface continued to exert an effect on adsorption, even though the RH of the carrier gas at the column

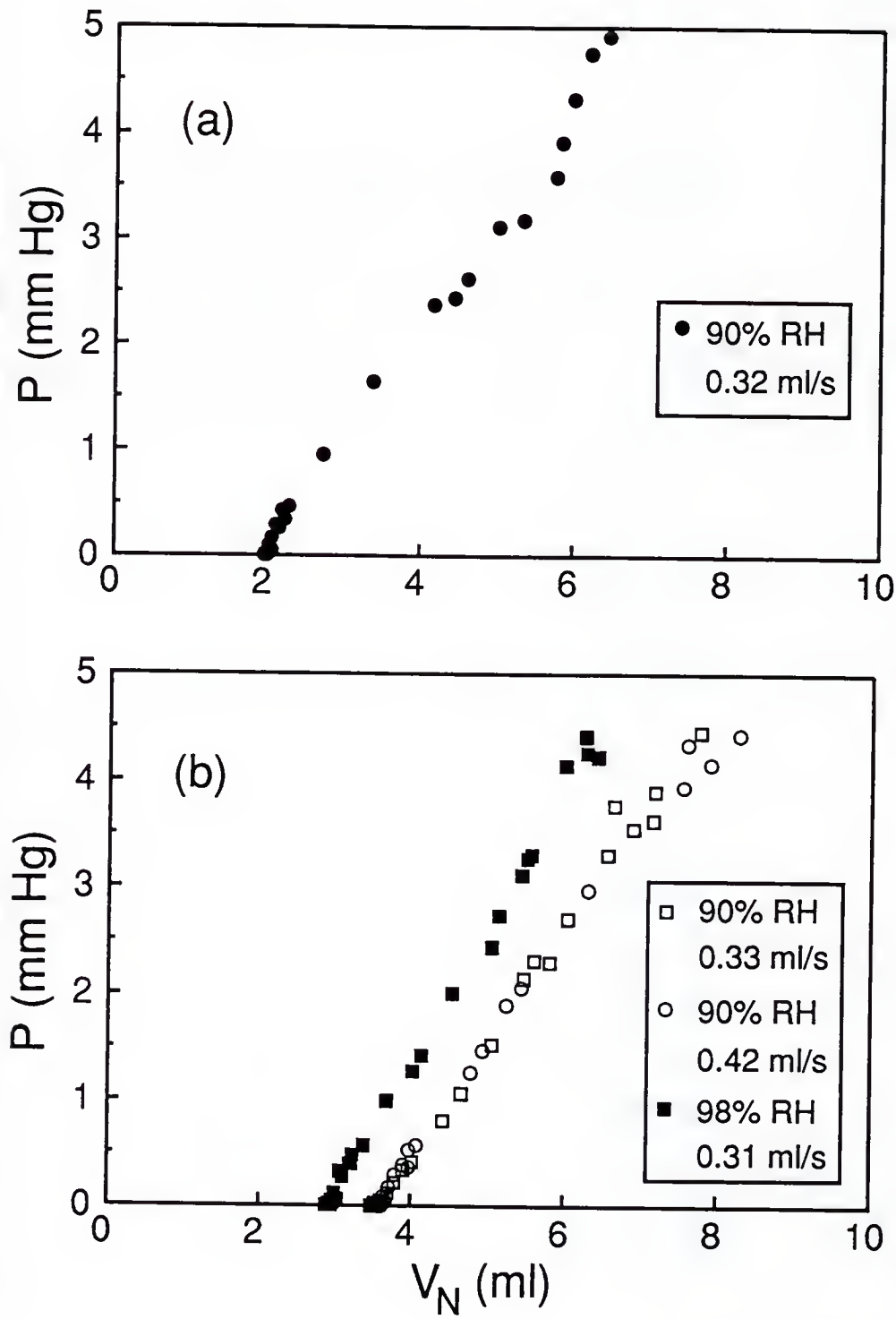

Figure 3-4. Chromatographic peak maxima at room temperature (≈ 24°C) for p-xylene vapor on (a) salt-treated Oldsmar soil at 90% RH and (b) untreated Oldsmar soil at 90 and 98% RH.

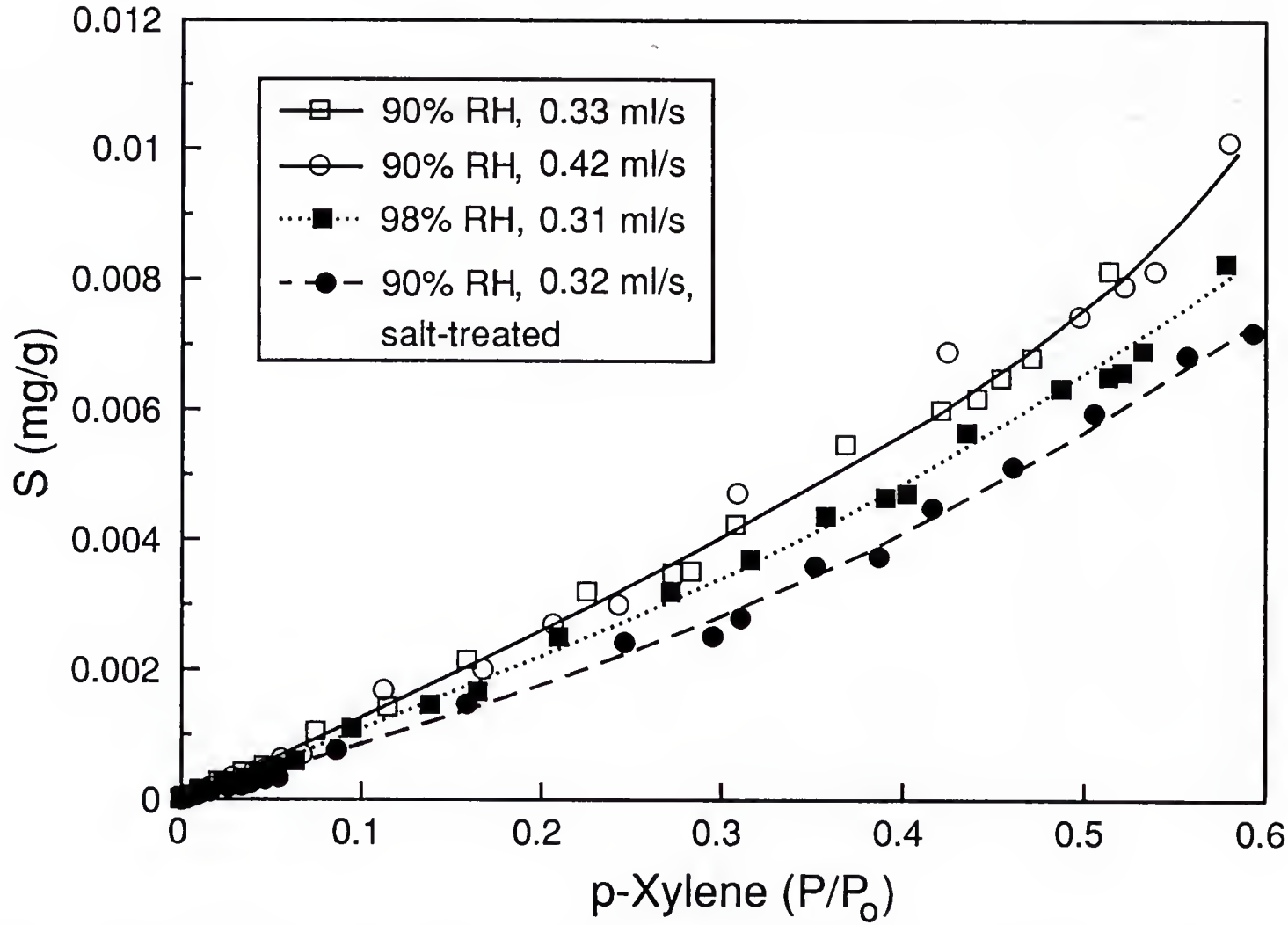

Figure 3-5. Adsorption isotherm for p-xylene vapor on salt-treated Oldsmar soil at 90% RH, and salt-treated Oldsmar soil at 90 and 98% RH.

inlet was 90%. Subsequent measurements revealed that inlet relative humidities of 90 and 98% corresponded to relative humidities at the column outlet of 60 and 70%, respectively. Since the back pressure measured at the column inlet ranged from only 1.04 to 1.07 atm, it was unlikely that the RH drop was due solely to pressure gradients. Apparently, the 8-hour equilibration period was not sufficient to completely hydrate the support. Future experiments will be conducted after equilibrating the columns for several days at 90% RH.

The presence of salt also reduced p-xylene adsorption on Oldsmar sand, which was consistent with batch data obtained for the sorption of p-xylene vapors on Webster soil and Webster HP at 90% RH (Figure 3-3b). Based on water adsorption data, the concentration of $CaCl_2$ in adsorbed water films of the Webster soils was approximately 1.0 M. To further investigate the adsorption at the gas-liquid interface, the surface tension of 1.0 M $CaCl_2$ exposed to p-xylene vapors was measured by the drop-weight method, as described in Chapter 2. These data were expressed as surface pressure (π), which is equivalent to the difference between the surface tension of the pure solution (γ_o) and the film-covered surface (γ) (Figure 3-6). The surface excess (Γ) can be calculated in the same manner as described in Chapter 2 by simply replacing γ in equation (2-7) with π (Blank and Ottewill, 1964). However, the data presented in Figure 3-6 indicated that the surface excess calculated for 1.0 M $CaCl_2$ and deionized water would be identical. This finding was consistent with the data of Blank and Ottewill (1964), who reported that the surface excess of benzene, toluene, and o-xylene on 0.1 M NaCl was similar to that obtained using distilled water. Thus, the surface tension

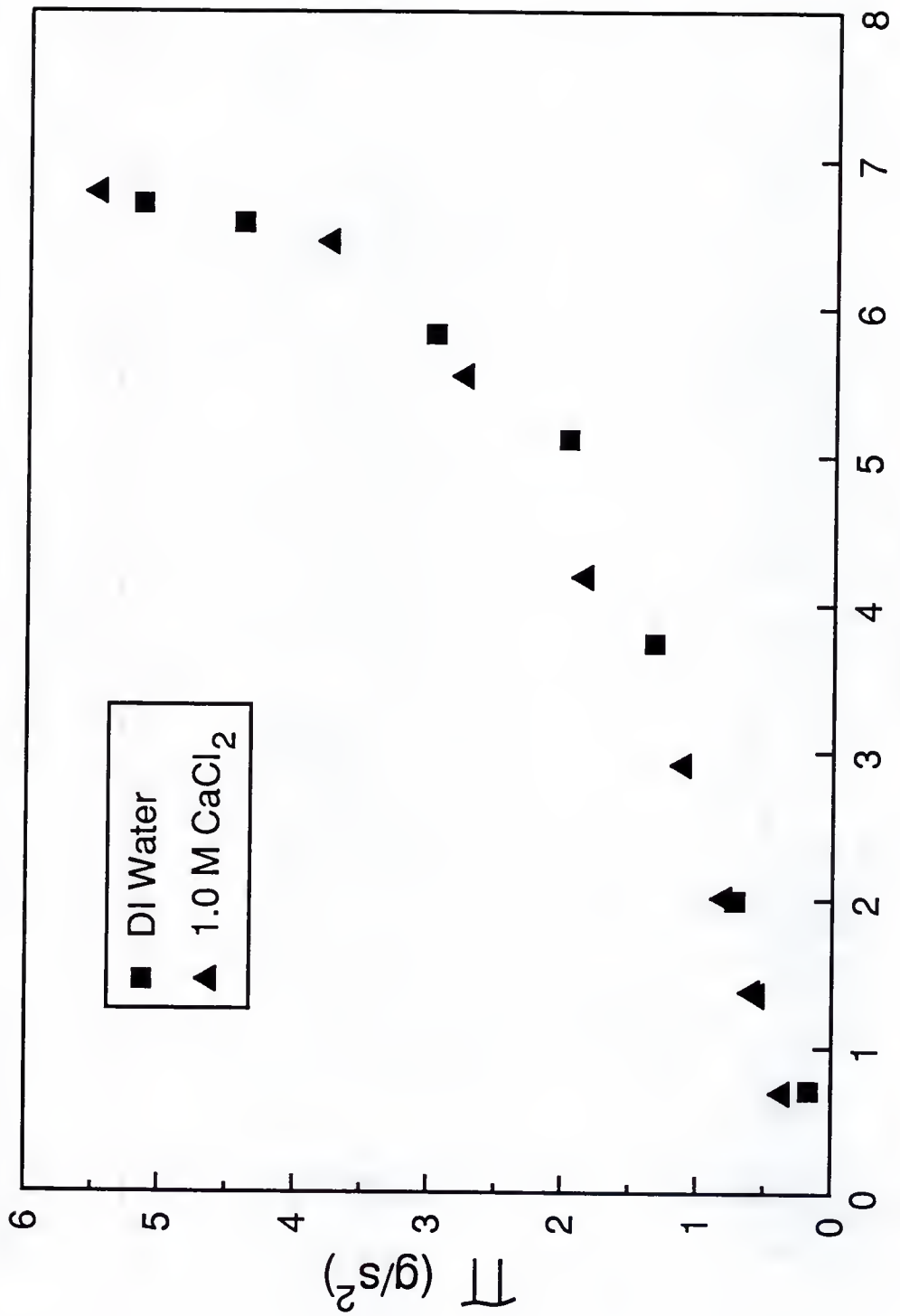

Figure 3-6. Surface pressure of deionized water and 1.0 M $CaCl_2$ exposed to p-xylene vapors at room temperature (≈24°C).

measurements suggested that the presence of salt would have no effect on the adsorption of p-xylene at the gas-liquid interface.

Summary

The measurement of vapor-phase adsorption on soil materials by batch techniques is typically an arduous task, requiring several time-consuming experiments in order to obtain an adsorption isotherm. In contrast, gas chromatography can be efficiently employed under a range of temperature and moisture regimes. Vapor-phase adsorption of p-xylene on Oldsmar sand was measured by the eluted-pulse method of Dorris and Gray (1981). Type-II isotherms obtained for p-xylene adsorption on anhydrous Oldsmar sand were in agreement with preliminary batch data. At high RH, adsorption isotherms shifted from Type-II to Type-III, and the magnitude of p-xylene adsorption was reduced. A similar effect has been observed for the sorption of several organic vapors on hydrated soils (Call,1957; Chiou and Shoup, 1985; Rhue et al., 1989). However, some difficulty was encountered at high RH, and it is recommended that the columns be equilibrated at 90% RH for several days. Additional experiments will be conducted at high RH, and batch experiments are planned to further verify GC data.

Salt treatments resulted in decreased p-xylene adsorption on anhydrous and hydrated Oldsmar sand. These data were consistent with batch studies of p-xylene adsorption on Webster soil and Webster HP exposed to $CaCl_2$, and suggest

that vapor-phase sorption will be significantly reduced in salt-effected soils. Under anhydrous conditions, the reduced adsorption capacity of salt-treated Oldsmar sand may have resulted from the formation of salt coatings on the sorbent surface. In Chapter 2 it was postulated that sorption on hydrated sorbents occurred by (1) partitioning into OC, (2) dissolution into adsorbed water films, (3) adsorption at the gas-liquid interface. Given the low solubility of p-xylene in water and the relatively low OC content of Oldsmar sand it is unlikely that any alteration of these components by salt would significantly effect adsorption. Thus, it was postulated that the salt-treatment reduced the adsorptive capacity of the gas-liquid interface. However, the surface concentrations of p-xylene on water and 1 M $CaCl_2$ calculated from measurements of the change in surface tension of deionized water and 1 M $CaCl_2$ exposed to p-xylene vapors were identical. This finding was somewhat puzzling, and prompted a reformulation of the Gibbs adsorption equation to account for three components (i.e., p-xylene, $CaCl_2$, and water). If the surface excess of water is assumed to be constant, the Gibbs equation can be expressed as:

$$\Gamma_1 = -\frac{1}{RT}\frac{d\gamma}{d\ln a_1} - \Gamma_2\frac{d\ln a_2}{d\ln a_1} \qquad (3\text{-}4)$$

where Γ_1 and Γ_2 are the surface concentrations of p-xylene and $CaCl_2$ (mol/cm^2), respectively, a_1 and a_2 are the activities of p-xylene and $CaCl_2$, respectively, R is the gas constant, and T is the temperature. This equation indicates that if $CaCl_2$ moved to the gas-liquid interface, it could compensate for any reduction in the

surface tension arising from the accumulation of p-xylene at the gas-liquid interface. Unfortunately, the surface concentration of $CaCl_2$ (Γ_2) was unknown, and thus it was impossible to calculate the surface concentration of p-xylene. This line of reasoning may explain why no difference was observed in the change in surface tension of water and $CaCl_2$ exposed to p-xylene vapors.

Additional studies indicated that the utility of GC techniques under anhydrous conditions may be limited to supports of low sorptive capacity. p-Xylene vapors injected on coated sands and kaolin were strongly adsorbed and eluted solute peaks were not discernable. Planned experiments will focus on the dilution of such sorbents, by either adding low-sorptive-capacity materials to the column or by coating sands with clay films. It should be recognized that batch studies are difficult to conduct for materials of low sorptive capacity and, thus, GC techniques are complimentary in this regard.

CHAPTER 4
COMPETITIVE ADSORPTION OF P-XYLENE AND WATER VAPORS ON CA-, NA-, AND LI-SATURATED KAOLIN

Introduction

Relative humidity (RH) or soil moisture content is one of the most important factors influencing the sorption of volatile organic chemicals (VOCs) in the unsaturated zone. Previous studies have demonstrated that water effectively competes with nonpolar organic vapors for mineral surfaces, resulting in the suppression of VOC sorption on soils and clay minerals. (Call, 1957; Chiou and Shoup, 1985; Rhue et al., 1989). This phenomenon has been attributed to the relatively strong interactions between water and mineral surfaces (Chiou and Shoup, 1985; Valsaraj and Thibodeaux, 1988), which may result from cation-dipole interactions, hydrogen bonding, and weak charge transfer interactions (Burchill et al., 1981). Of particular interest is cation hydration, the energy of which has been directly related to the degree of water adsorption on kaolinite (Keenan et al., 1951; Jurinak, 1963). However, the effect of exchangeable cations on the competitive adsorption of water and organic vapors is largely unknown. In addition, models capable of predicting vapor-phase adsorption from binary systems have rarely been tested due, primarily, to the lack of suitable data.

Cation saturation has been shown to indirectly effect the competitive adsorption of water and ethylene dibromide (EDB) vapors by altering the surface area of montmorillonite. Following exposure to P_2O_5, Jurinak (1957) observed that water retention by Mg-, Ca-, and Na-saturated montmorillonite was directly related to the hydration energy of the exchangeable cation. The retained water expanded the interlayer space, and thus Mg-montmorillonite exhibited the greatest surface area and EDB adsorption, followed by Ca- and Na-montmorillonite. A similar phenomenon was noted by Call (1957), who reported that EDB sorption on Ca-saturated montmorillonite was greater at 5, 10 and 20% relative humidity (RH) than at 0% RH (Figure 4-1). This effect was attributed to expansion of the clay lattice, which increased from 3Å at 0% RH to 9Å at 5-10% RH. Apparently, EDB molecules were only able to enter the interlayer space after the clay lattice had expanded to 9Å. However, as the number of water molecules continued to increase, competition between EDB and water became greater, resulting in the suppression of EDB adsorption.

Although these data clearly demonstrate that cation saturation influenced EDB adsorption on montmorillonite, the effect of specific interactions between water and exchangeable cations was obscured by changes in surface area. In addition, Jurinak (1957) reported that montmorillonite forms porous aggregates or floccules during dehydration. This process, which has been observed by electron micrography (Grim, 1953), restricted the adsorption of EDB on Mg-, Ca-, and Na-montmorillonite (Jurinak, 1957). In contrast, EDB adsorption on kaolinite occurred

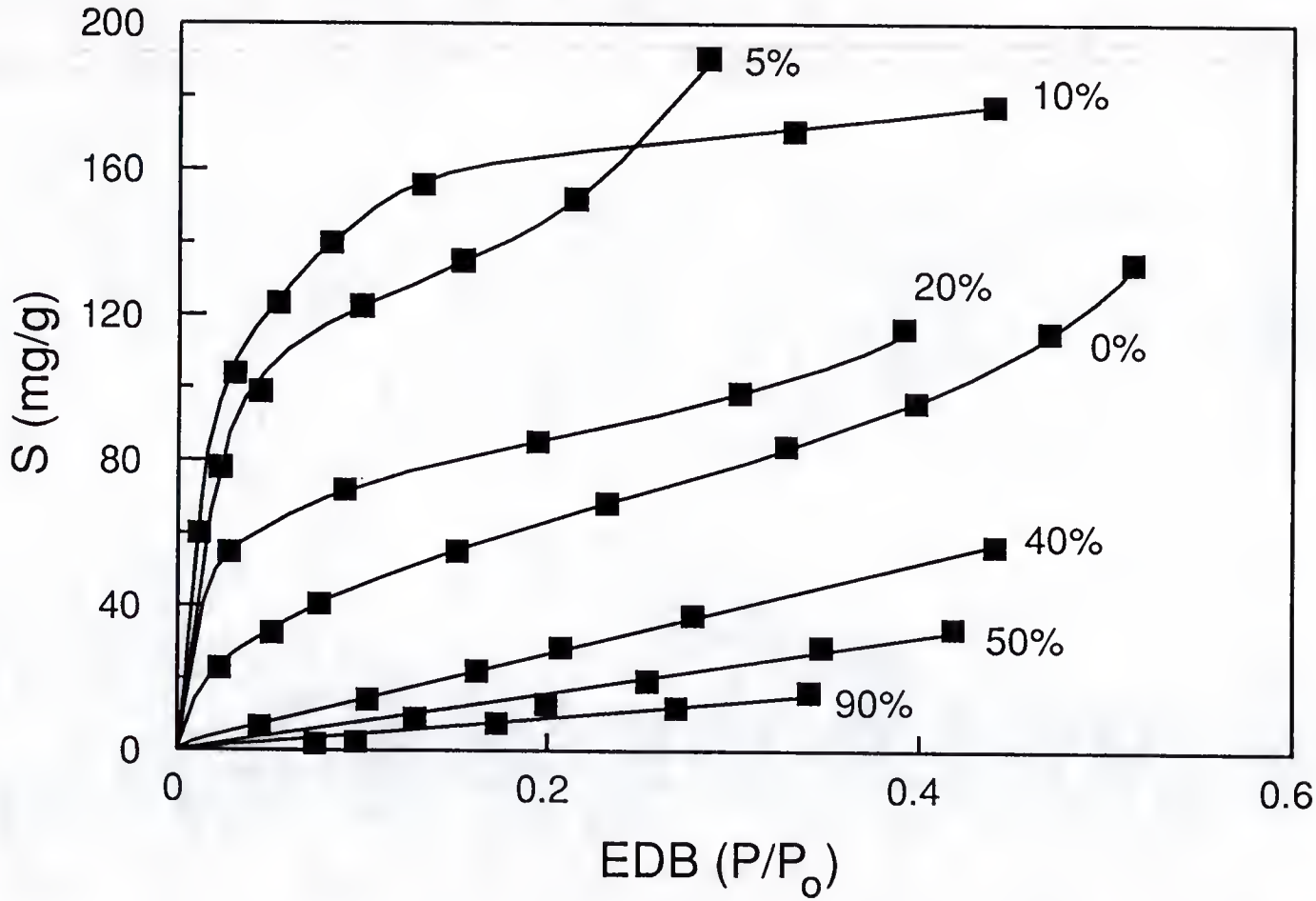

Figure 4-1. Vapor-phase adsorption of EDB on Ca-saturated montmorillonite at various RH (Call, 1957).

on free surfaces or in pores whose size was far greater than that of the EDB molecule. Thus, kaolin appears to provide a surface absent of surface area and porosity effects which complicated the interpretation of EDB adsorption on montmorillonite.

Recently, Rhue et al. (1989) used a methanol extraction procedure to simultaneously measure water and p-xylene adsorption on predominantly Na-saturated kaolin. At low RHs and relatively high p-xylene vapors pressures, Rhue et al. (1989) observed enhanced water adsorption based on comparisons between measured and predicted data. The predicted values were calculated using a modified Brunauer, Emmett, and Teller (BET) equation which accounted for two adsorbate species. The purpose of this study was to determine if the preferential adsorption of water could be attributed cation hydration effects. Initially, single-adsorbate isotherms were obtained for p-xylene and water vapor adsorption on Ca-, Na-, and Li-kaolin. The linear form of BET equation was utilized to obtain the monolayer adsorption capacity and value of C. These data were then used to predict competitive adsorption of p-xylene and water vapors based on the two-component BET equations of Hill (1946a, b) and Rhue et al. (1989).

Materials and Methods

Kaolinite Samples

Colloidal kaolin, obtained from Fisher Scientific Products (K-6, Lot# 731063), used in this study was identical to that described in Chapter 2. The kaolin had a

cation exchange capacity (CEC) of 4.2 $cmol_c/kg$ at pH 5.5, and was predominantly Na-saturated with trace amounts of Ca, Mg, and K (Rhue et al., 1989). Prior to adsorption experiments, the kaolin was washed with 1 M NaAOc buffered to pH 4.11 with acetic acid to remove carbonates. Approximately 2.5 g of kaolin was placed in individual polyethylene centrifuge tubes, to which 20 mL of 1 M NaAOc was added. The samples were mixed until the kaolin was completely dispersed, and separated by centrifugation at 2500 rpm for 5 minutes. When the pH of the supernatant was less than 5.0, generally after one wash, the kaolin was washed five times with 1 M NaCl to removed entrained NaAOc. The supernatant was analyzed for Ca and Mg using a Perkin Elmer model 603 atomic absorption spectrophotometer. If either Ca or Mg was detected in the supernatant, the NaAOc treatment was repeated, otherwise the kaolin was saturated with the desired cation.

Ca-, Na-, and Li-saturated Fisher kaolin was prepared by washing the kaolin with the appropriate 1 M chloride salt until no other cations could be detected in the supernatant by atomic absorption spectroscopy. Following cation saturation, the kaolin was repeatedly washed with 95% ethanol until a negative chloride test was achieved using $AgNO_3$. The kaolin was air-dried at room temperature and ground with an agate motar and pestal. Prior to adsorption experiments, the kaolin was oven-dried at approximately 120°C for at least two weeks. The N_2 surface area of Ca, Na, and Li-kaolin was 15.8, 15.6, and 15.5 m^2/g, respectively, prior to

heating, and 15.5, 15.4, and 15.2 m^2/g, respectively, after heating (Advanced Materials Research Center, University of Florida).

Vapor-Phase Adsorption Experiments

Single and mixed-vapor adsorption experiments were conducted at 24°C using the flow-equilibration apparatus described in Chapter 2. The concentration of water in the flow stream was determined by Karl Fisher (KF) titration. Approximately 20 mL of $CaCl_2$-saturated methanol was added to two 40 mL glass centrifuge tubes, and pretitrated to the visual KF endpoint. The tubes were placed on the flow stream in series, via hypodermic needles, for a measured time period. The solutions were then removed from the flow stream and immediately retitrated. A small amount of titer was consistently needed to retitrate the second trap in the series, which was attributed to loss of volatile compounds from the KF reagent (Rhue et al., 1988). Therefore, the volume of titer used for the second trap was subtracted from that of the first trap, and the corrected value was used to calculate the amount of water trapped in the methanol. p-Xylene vapors were trapped by bubbling the flow stream through two glass centrifuge tubes containing methanol, as described in Chapter 2.

Single-adsorbate isotherms were determined for p-xylene and water vapors at relative vapor pressures ranging from 0.1 to 0.5. The competitive adsorption of p-xylene and water vapors was measured at 10 and 20% RH. Adsorbed concentrations of p-xylene and water vapors from single- and binary- sorbate systems were measured following the procedures described previously.

Preliminary Adsorption Experiment

A preliminary study was conducted to test the effect of cation saturation on the competitive adsorption of water and p-xylene vapors on kaolin. A portion of the original Fisher kaolin was saturated with Li by washing the kaolin with 1 M LiCl. Excess salt was removed by repeatedly washing the kaolin with 95% ethanol until a negative chloride test was achieved with $AgNO_3$. The adsorption of water and p-xylene vapors on Na- and Li-saturated kaolin was measured for single- and binary-sorbate systems as described previously.

Results and Discussion

Preliminary Adsorption Experiment

Water adsorption on Na-kaolin was in agreement with the data obtained by Rhue et al. (1989), and was significantly greater than that on Li-kaolin (Figure 4-2a). In contrast, p-xylene adsorption on Na- and Li-kaolin was similar (Figure 4-2b), suggesting that exchangeable cations had only a minor effect on p-xylene adsorption. The adsorption data were fit by a least squares procedure to the linear form of the BET equation,

$$\frac{P/P_o}{S(1-P/P_o)} = \frac{1}{S_mC} + \frac{(C-1)P/P_o}{S_mC} \qquad (4\text{-}1)$$

where S_m is the monolayer adsorption capacity (mg/g), and C is a parameter related to the heat of adsorption. Estimated values of S_m and C are presented in Table 4-1. BET parameters for Na-kaolin were calculated using a combined data

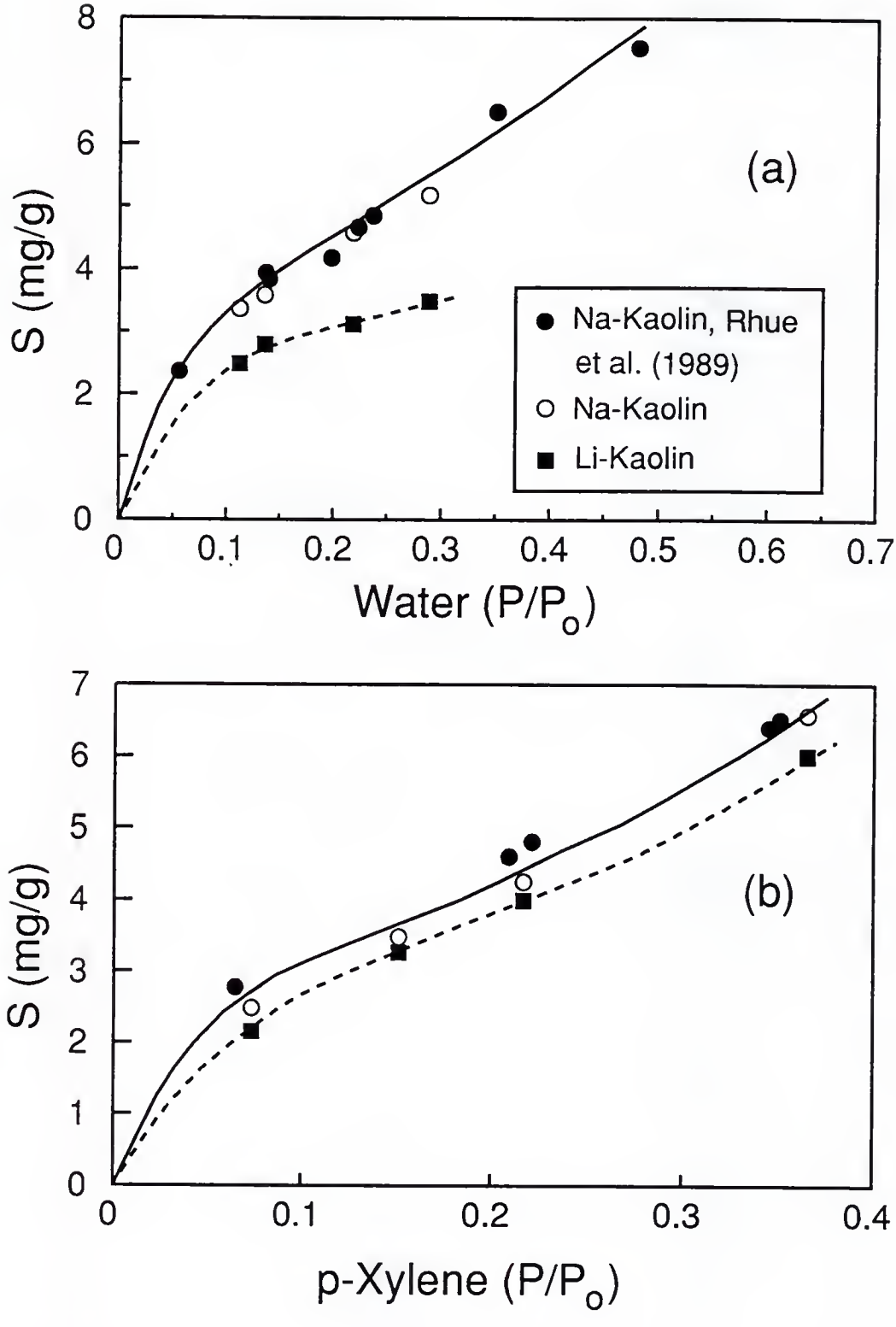

Figure 4-2. Vapor-phase adsorption of (a) water and (b) p-xylene on Na- and Li-saturated Fisher kaolin at 24°C.

Table 4-1. BET parameters for Na- and Li-kaolin calculated from single-sorbate isotherm data (Rhue et al., 1989).

Sorbent	Sorbate	S_m	C	r^2	P/P_o Range Used
		-mg/g-			
Na-kaolin	p-xylene	4.5	14	0.969	0.065-0.424
	water	4.2	20	0.988	0.056-0.481
Li-kaolin	p-xylene	4.4	9	0.997	0.074-0.365
	water	2.6	52	0.997	0.112-0.289

set, since the values obtained for water and p-xylene adsorption were similar to those reported by Rhue et al. (1989).

The monolayer adsorption capacity of water on Li-kaolin was considerably less than that on Na-kaolin. It has been proposed that exchangeable Na on kaolin hydrates readily; whereas, exchangeable Li does not hydrate, despite the fact that Li has a slightly greater hydration energy than Na (Keenan et al., 1951). Apparently, Li ions form inner-sphere complexes or are strongly adsorbed on kaolin, such that hydration does not occur even at high RHs (Keenan et al., 1951; Martin, 1959). If the amount of water adsorbed by Li-kaolin is considered to be independent of cation hydration effects, then the difference between the monolayer adsorption capacities of Na- and Li-kaolin provides an estimate of the amount of water hydrating Na. Based on this assumption, approximately 1.8 molecules of water were associated with each exchangeable Na ion, which was consistent with the range of values (1.5 to 1.8 molecules of water) reported by Keenan et al. (1951) for Na-, K-, and Rb-saturated kaolinite.

The binary-vapor experiment was conducted at p-xylene and water relative vapor pressures of 0.395 and 0.095, respectively. The amount of water and p-xylene adsorbed on Na-kaolin in this experiment was 2.46 (±0.00) and 6.56 (±0.05) mg/g, respectively. In contrast, Li-kaolin adsorbed 2.06 (±0.01) and 6.04 (±0.05) mg/g of water and p-xylene, respectively. Rhue et al. (1989) modified the BET equation to account for the competitive adsorption of two sorbate species. The

total adsorbed mass of sorbate "a" on the surface (M_a, mg/g) can be calculated using the following equation:

$$M_a = \alpha_a C_a S_o [X_a/(1-X_a)^2] \quad (4\text{-}2)$$

where α is the mass of compound "a" occupying a unit area of surface (mg/m^2), C_a is the BET parameter related to heat of adsorption calculated from single-vapor adsorption isotherm for sorbate "a", X_a is the relative vapor pressures of sorbate "a", and S_o is the area of exposed surface area per unit mass of adsorbent (m^2/g). The α values for water and p-xylene were calculated to be 0.31 and 0.50 mg/m^2, respectively, based on the following equation:

$$\alpha = 1.091(MW/a_m A) \quad (4\text{-}3)$$

where MW is the molecular weight, a_m is the cross-sectional area of sorbate determined in Chapter 2, and A is Avogadro's number (Rhue et al., 1989). The mass of sorbate "b" (M_b) can be calculated in a similar manner. Unfortunately, the mass of either adsorbate on the surface cannot be calculated because S_o is unknown in the binary vapor system (Rhue et al., 1989). However, the fraction of adsorbate "a" (F_a) on the surface can be calculated using the following equation:

$$F_a = \frac{M_a}{M_a + M_b}. \quad (4\text{-}4)$$

The calculated versus the measured fraction of water adsorbed on Na-kaolin (Na) and Li-kaolin (Li) are presented in Figure 4-3. These data indicate that Na-kaolin adsorbed considerably more water than was predicted by the two-component BET equation. The fraction of water adsorbed on Na-kaolin was previously reported by

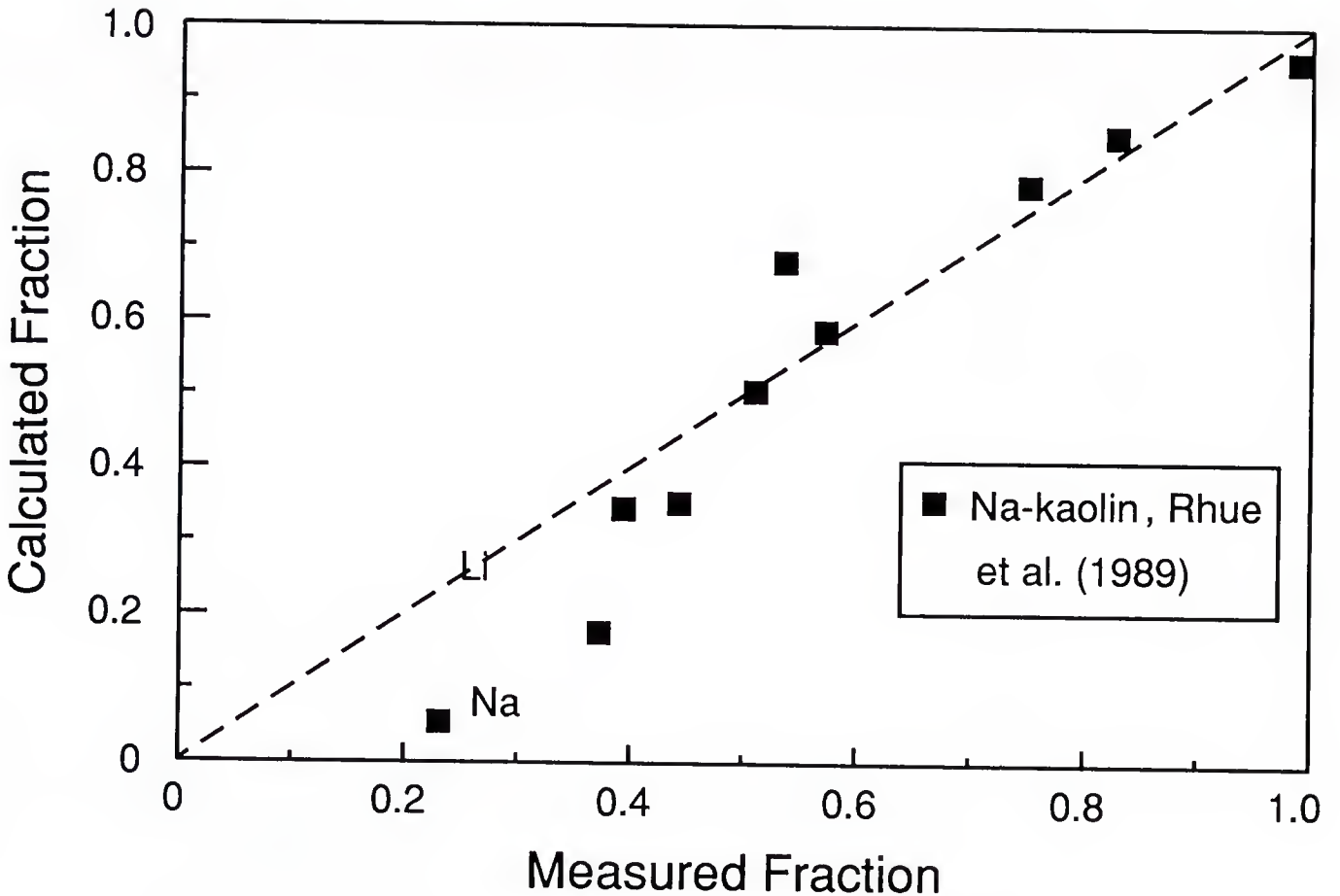

Figure 4-3. Measured fraction of water adsorbed on Na- (Na) and Li-saturated (Li) Fisher kaolin versus the fraction predicted using the multi-sorbate BET equation of Rhue et al. (1989).

Rhue et al. (1989), and is denoted by (■) in Figure 4-3. In contrast, the measured and calculated fractions of water adsorbed on Li-kaolin were almost identical. These data suggest that the preferential adsorption of water relative to p-xylene at low water fractions (below 0.4) was due to Na hydration.

One possible explanation for the difference between the measured and calculated fraction of water adsorbed on Na-kaolin was the similarity in the values of C estimated from water and p-xylene single-sorbate isotherms. Since the values of C were essentially the same, the two-component BET equation of Rhue et al. (1989) did not account for preferential adsorption of water over p-xylene on Na-kaolin. In contrast, the values of C for water and p-xylene adsorption on Li-kaolin were 52 and 9, respectively. The large value of C for water adsorption on Li-kaolin was not anticipated, because Li-kaolin is generally considered to represent a mineral surface free of cation hydration effects. If a C value of 20 was used to estimate the mass of water adsorbed on Li-kaolin, then the calculated fraction of water adsorbed on Li-kaolin would be 0.12 rather than 0.28. Thus, Li-kaolin would also have exhibited a small degree of preferential water adsorption if the measured value of C had been in the range expected for water adsorption on Fisher kaolin.

Vapor-Phase Adsorption on Ca-, Na-, and Li-kaolin

Isotherms for the adsorption of water vapor on Ca-, Na-, and Li-kaolin are presented in Figure 4-4a. Ca-kaolin adsorbed the greatest amount of water at all RHs studied, followed by Na- and Li-kaolin. The monolayer adsorption capacities

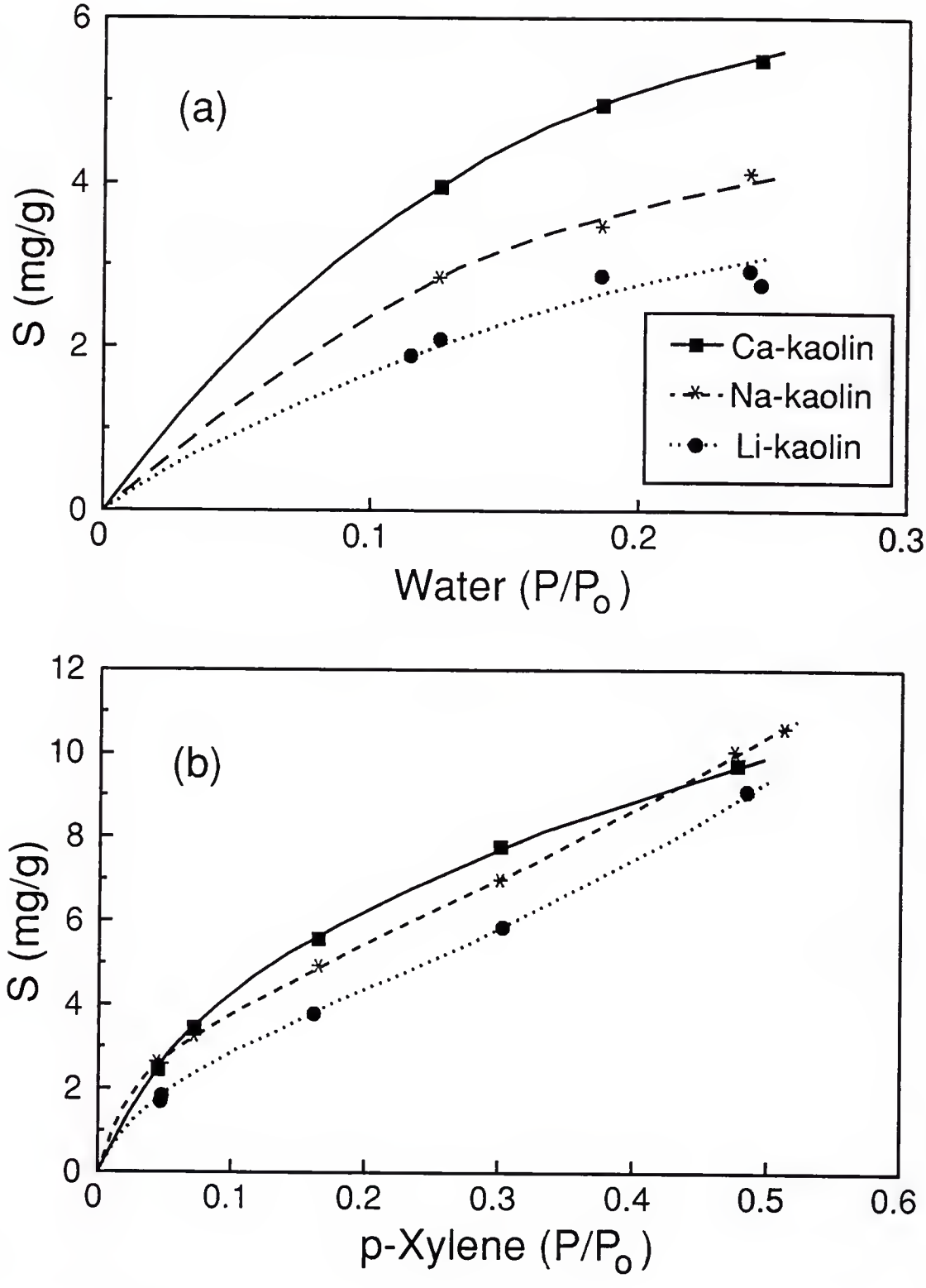

Figure 4-4. Vapor-phase adsorption of (a) water and (b) p-xylene on Ca-, Na-, and Li-saturated Fisher kaolin at 24°C.

of water on Ca-, Na-, and Li-kaolin derived from the single-sorbate adsorption data were 5.0, 3.9, and 2.8 mg/g, respectively (Table 4-2). These data indicate that cation saturation had a considerable effect on water adsorption, and were similar to values of S_m obtained for Na- and Li-kaolin in the preliminary study. The value of C for water adsorption on Li-kaolin (12) was less than that measured previously, but was now within the range expected for water adsorption on Fisher kaolin. Thus, the value of C was subject to uncertainty, even when the value of S_m derived from the same adsorption data appeared to give a reasonable estimate of the monolayer adsorption capacity. The reasons for uncertainty in the value of C are unclear, but the evaluation of numerous adsorption isotherms indicates that small differences in adsorption data can result in substantial changes in the value of C, particularly if the isotherm consists of only a few data points.

In general, Ca-kaolin adsorbed the largest amount of p-xylene, followed by Na- and Li-kaolin (Figure 4-4b). However, p-xylene adsorption on Na-kaolin was slightly greater than that on Ca-kaolin at relative vapors pressures below 0.05 and above 0.5. The p-xylene monolayer adsorption capacities of Ca-, Na-, and Li-kaolin were 6.5, 5.5, and 5.0 mg/g, respectively (Table 4-2). These data indicate that cation saturation influenced the adsorption of p-xylene vapors, but the similarity between the values of S_m indicates that the effect of cation saturation was minimal. In order to compare the monolayer adsorption capacities for water and p-xylene, the value of S_m was expressed as the amount of surface occupied by sorbate molecules per gram of kaolin (m^2/g), as described in Chapter 2 (Table 4-

Table 4-2. BET parameters for Ca-, Na- and Li-kaolin calculated from single-sorbate isotherm data.

Sorbent	Sorbate	S_m	C	r^2	S_{mA}	P/P_o Range Used
		-mg/g-			-m^2/g-	
Ca-kaolin	p-xylene	6.5	12	0.999	14.0	0.045-0.301
	water	5.0	17	0.993	17.6	0.126-0.245
Na-kaolin	p-xylene	5.5	16	0.998	11.9	0.044-0.301
	water	3.9	12	0.978	13.7	0.126-0.241
Li-kaolin	p-xylene	5.0	10	0.997	10.8	0.047-0.303
	water	2.8	12	0.994	9.8	0.115-0.241

2). The BET surface areas determined in this manner indicate that when the molecular weight and surface packing are taken into consideration, the p-xylene monolayer adsorption capacities were less than those measured for water. In addition, the effect of the saturating cation and CEC the BET surface areas were also smaller than that observed for water.

In order to utilize the method of Keenan et al. (1951) for estimating the amount of water and p-xylene associated with exchangeable cations, the CEC of kaolin used in the adsorption experiments was measured. The CEC of oven-dried Ca-, Na-, and Li-kaolin at pH 4.11 was 3.9, 3.5, and 1.9 $cmol_c/kg$, respectively. To confirm these values, the CEC of the kaolin used in the preliminary adsorption study was also measured. At pH 5.5, the CEC of oven-dried Na- and Li-kaolin was 4.23 and 2.19 $cmol_c/kg$, respectively. Apparently, the heat-treatment resulted in a sizable reduction in the CEC of Li-kaolin. These findings suggest that heat-treated Li-kaolin represents a mineral surface of reduced charge, rather than a surface free of cation hydration effects as proposed by Keenan et al. (1951) and Martin (1959). Therefore, the use of Li-kaolin as a reference mineral surface may not be valid, and could result in incorrect estimates of the amount of water associated with each exchangeable cation.

Competitive Adsorption of p-Xylene and Water on Ca-, Na-, and Li-kaolin

Data for the adsorption of p-xylene vapors on Ca-, Na-, and Li-kaolin at 0, 10, and 20% RH are presented in Figure 4-5. An increase in RH from 0% to 10 and 20% had a relatively minor effect on p-xylene adsorption regardless of the

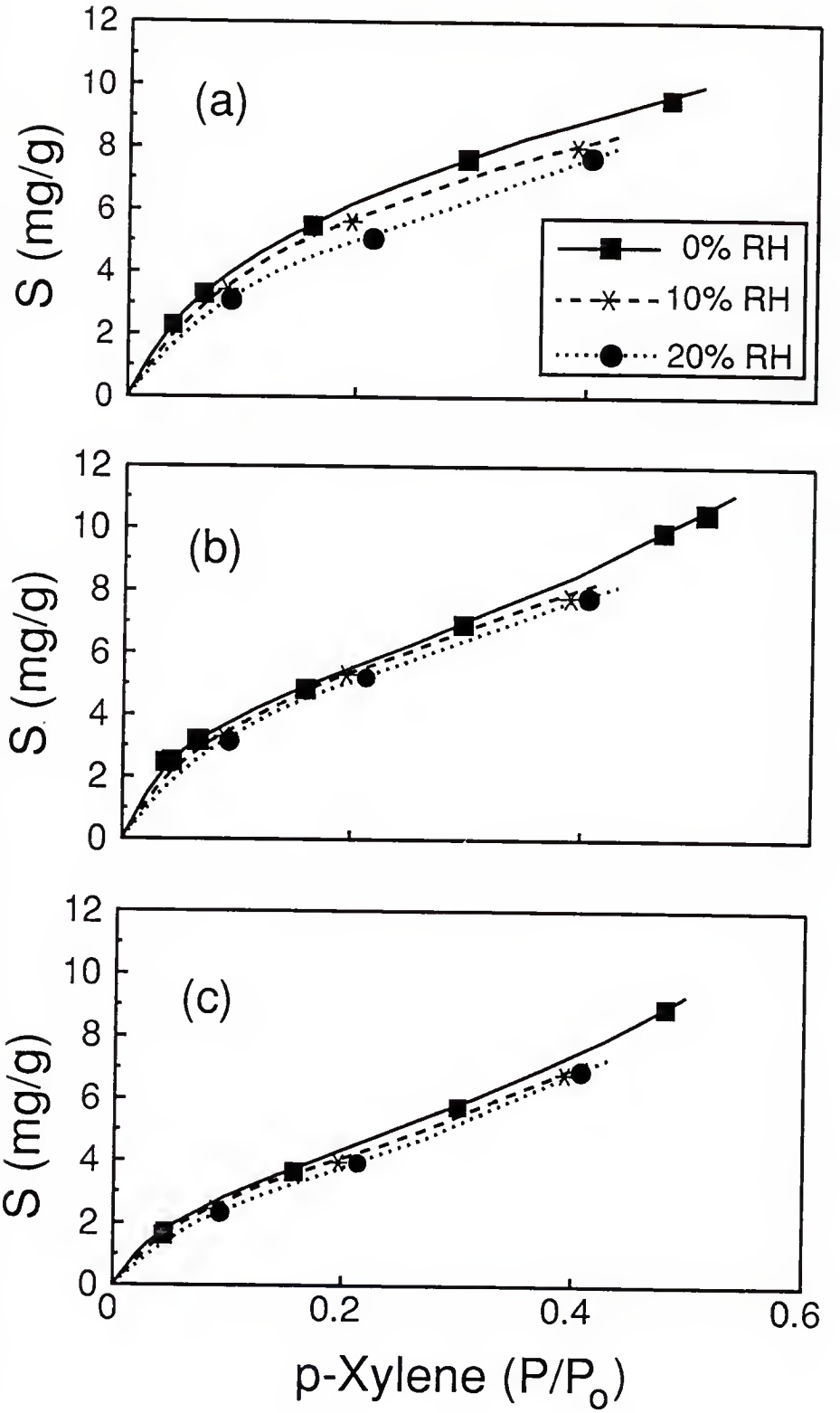

Figure 4-5. Vapor-phase adsorption of p-xylene on (a) Ca-, (b) Na-, and (c) Li-saturated Fisher kaolin at 0, 10, and 20% RH.

cation saturation. Rhue et al. (1989) reported that sizable reductions in p-xylene adsorption were not observed until the RH was greater than that required to attain monolayer water coverage, as estimated from the single-sorbate BET equation. The RHs corresponding to monolayer coverage of water on Ca-, Na-, and Li-kaolin were 20, 22, and 22%. Thus, the slightly greater displacement of p-xylene from Ca-kaolin was consistent with the fact that a lower RH was required to achieve monolayer coverage on Ca-kaolin than on Na- and Li-kaolin.

The measured fraction of water adsorbed on Ca-, Na-, and Li-kaolin, versus the fraction calculated from the two-component BET equation of Rhue et al. (1989), is presented in Figure 4-6a. Below 0.4, enhanced water adsorption was exhibited by all exchangeable cations studied, but was less for Li-kaolin than Ca- and Na-kaolin. The degree of preferential water adsorption was consistent with the CEC values previously reported for oven-dried Ca-, Na-, and Li-kaolin. These data further support the contention that Li-kaolin represents a surface of reduced charge.

The fraction of water adsorbed on kaolin was also predicted using the two-component BET equation proposed by Hill (1946a, 1946b). If the sorbate is assumed to adsorb only onto the mineral surface or sorbed layers of itself, Hill's equation can be simplified to:

$$\frac{S_a}{S_{am}} = \frac{X_a\,[C_a\,(1-X_b) + X_b C_b]}{(1 - X_a - X_b)\,[1 + X_a(C_a-1) + X_b(C_b-1)]} \qquad (4\text{-}5)$$

where S_a is the amount of sorbate "a" adsorbed (mg/g), S_{am} is the monolayer

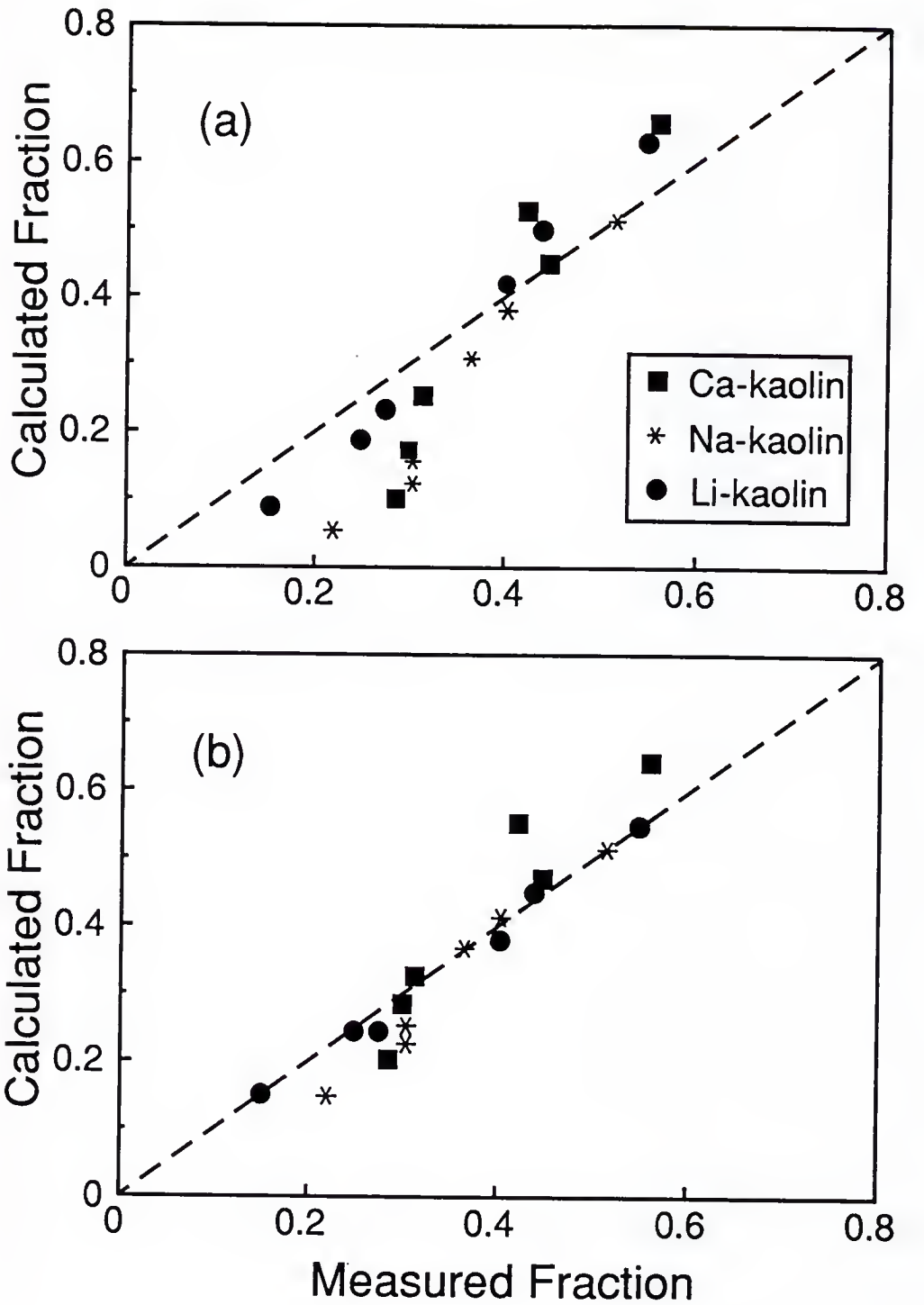

Figure 4-6. Measured fraction of water adsorbed on Ca-, Na-, and Li-saturated Fisher kaolin versus the fraction calculated using the two-component BET equation of (a) Rhue et al. (1989), and (b) Hill (1946a, b).

adsorption capacity of sorbate "a" (mg/g), X_a and X_b are the relative vapor pressures of sorbate "a" and "b", respectively, and C_a and C_b are the BET parameters related to the heat of adsorption of sorbate "a" and "b", respectively. The predicted adsorption of water and p-xylene on Ca-, Na-, and Li-kaolin is presented in Table 4-3. The adsorption of water and p-xylene on kaolin was well predicted, regardless of the cation saturation. However, the predicted values for Li-kaolin were more accurate than those estimated for Ca- and Na-kaolin.

The measured fraction of water adsorbed on Ca-, Na-, and Li-kaolin versus the fraction predicted using the two-component BET equation of Hill (1946a, 1946b) are presented in Figure 4-6b. The measured and calculated fractions of water adsorbed on Li-kaolin were similar for all mixed-vapor systems studied. At fraction less than 0.3, Ca- and Na-kaolin exhibited enhanced water adsorption. However, the magnitude of the preferential water adsorption observed here was far less than that obtained using the two-component BET equation of Rhue et al. (1989). This was primarily due to the fact that Hill's two-component BET equation incorporates the value of S_m, determined from single-sorbate adsorption isotherms. Thus, the adsorption of water and p-xylene predicted by Hill's equation is based, in part, on the monolayer adsorption capacity of each sorbent. In contrast, the equation of Rhue et al. (1989) does not include a monolayer adsorption capacity term. Therefore, the value of C must be related to the cation hydration energy in order for the fraction of water calculated using the two-component BET equation to reflect differences in the monolayer adsorption capacity due to cation saturation.

Table 4-3. Comparison of measured p-xylene and water adsorption on Ca-, Na-, and Li-kaolin from mixed-vapor systems with values predicted using the multi-sorbate BET equation of Hill (1946a, 1946b).

Sorbent	P/Po		Measured		Predicted	
	Water	PX	Water	PX	Water	PX
	mg/g					
Ca-kaolin	0.117	0.093	2.64	3.58	3.06	2.51
	0.101	0.201	2.64	5.72	2.34	4.88
	0.112	0.395	3.24	8.00	2.33	9.17
	0.179	0.096	4.13	3.22	4.07	2.28
	0.212	0.217	4.18	5.14	4.26	4.79
	0.184	0.403	3.42	7.89	3.91	9.80
Na-kaolin	0.117	0.093	2.31	3.40	1.93	2.75
	0.101	0.201	2.38	5.42	1.42	4.84
	0.112	0.395	2.27	7.94	1.47	8.45
	0.179	0.096	3.56	3.32	2.71	2.54
	0.212	0.217	3.09	5.33	2.82	4.84
	0.218	0.410	3.48	7.89	3.28	9.67
Li-kaolin	0.117	0.093	2.02	2.57	1.56	1.91
	0.101	0.201	1.56	4.09	1.21	3.71
	0.112	0.395	1.24	6.85	1.23	7.04
	0.179	0.096	2.93	2.39	2.13	1.77
	0.212	0.217	2.72	3.99	2.28	3.72
	0.218	0.410	2.34	6.97	2.61	8.08

However, Keenan et al. (1951) noted that the value of C, estimated from water adsorption on a series of alkali-saturated kaolin samples, ranged from 10 to 40 and showed no correlation with the properties of the exchange cation.

The utility of the two-component BET equation of Rhue et al. (1989) was also limited by uncertainty in the value of C. As noted previously, the C parameter obtained for Li-kaolin varied considerably even though the value of S_m appeared to be reasonable. This type of behavior was also observed for Na-kaolin. The calculated fraction of water adsorbed on Na-kaolin using the two-component BET equation of Rhue et al. (1989) at different values of C for water (C_w) is presented in Figure 4-7. For a p-xylene C value (C_{px}) of 16, the calculated fraction of water become larger as the value of C_w was increased. The value of C_w (12) determined from the single-sorbate isotherm was consistent with the value required for the calculated and measured fractions of water to agree for fractions greater than 0.4. When the value of C_{px} was decreased, the calculated fraction of water shifted to larger values, and separation between the curves increased (Figure 4-7b). These data indicate that the calculated fraction of adsorbed water predicted by the two-component BET equation of Rhue et al. (1989) was extremely sensitive to changes in the value of C for both water and p-xylene.

Summary

The data presented here indicate that vapor-phase adsorption of water on kaolin was a function of both the saturating cation and CEC of the kaolin. The

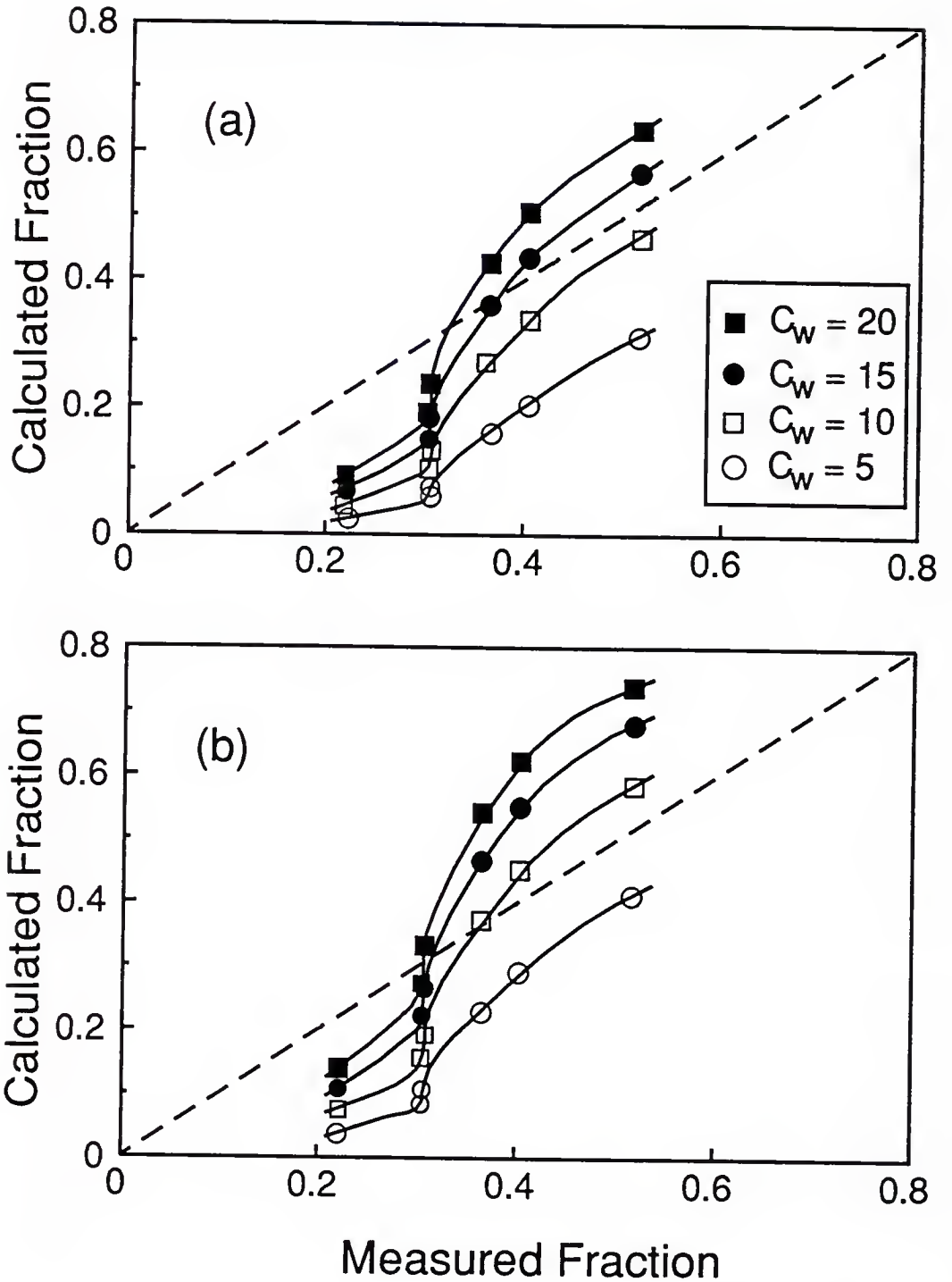

Figure 4-7. The effect of different values of C for water (C_w) on the fraction of water adsorbed on Na-kaolin using the two-component BET equation of Rhue et al. (1989) at values of C for p-xylene of (a) 16, and (b) 10.

amount of water adsorbed on Ca- and Na-kaolin was directly related to the hydration energy of the exchangeable cation. In contrast, Li-kaolin adsorbed considerably less water than Na-kaolin even though the hydration energy of Li is slightly greater than that of Na. This phenomenon has been reported previously, and was attributed to the absence of Li hydration (Keenan et al., 1951; Martin, 1959). However, Li-kaolin exhibited a 50% reduction in CEC after drying at 120°C, suggesting that the reduced water adsorption observed for Li-kaolin was due to a decrease in CEC. Thus, Li-kaolin may represent a surface of reduced charge, rather than a reference surface, free of cation hydration effects. The specific mechanisms responsible for charge reduction, and its effect on the hydration properties of Li-kaolin will be addressed in Chapter 5.

The effect of the saturating cation and CEC of kaolin on p-xylene adsorption were similar, but to a lesser extent, than that observed for water. These data suggest that specific interactions occurred between p-xylene molecules and exchangeable cations, which has not been reported previously. It was hypothesized that vapor-phase adsorption of p-xylene on kaolin can be characterized by weak interactions at cation exchange sites and physical adsorption (e.g., dipole-dipole interactions) on the remaining mineral surface. Since the energy of adsorption would be similar at these locations, p-xylene adsorption may approach "theoretical" monolayer coverage prior to the onset of multilayer formation. In contrast, water adsorption at low RHs is likely to be concentrated at cation exchange sites, resulting in the formation of discrete

patches of water. As the RH increases, multilayer formation would occur on hydrated cations along with adsorption on the remaining exposed mineral surface.

Increasing the RH from 0% to 10 and 20% resulted in small but successive decreases in p-xylene adsorption on Ca-, Na-, and Li-kaolin. Although competition between p-xylene and water vapors was evident at low RHs, kaolin exhibited a sizable capacity to adsorb p-xylene. These data suggest that exposed mineral surfaces were available for p-xylene adsorption, even at RHs approaching those required to attain monolayer water coverages. This rationale is consistent with the proposed existence of discrete regions of multilayer water adsorption and exposed mineral surfaces on kaolin at low surface coverages. Measured fractions of water adsorbed on Ca-, Na-, and Li-kaolin deviated from those calculated by the two-component BET equation of Rhue et al. (1989) at fractions less than 0.4. The observed difference could be attributed, in part, to the similarity in the values of C determined from p-xylene and water adsorption isotherms. In addition, uncertainty in the value of C limited the utility of the two-component BET equation of Rhue et al. (1989). In contrast, the two-component BET equation of Hill (1946a, b) incorporates both the S_m and C parameters determined from single-sorbate adsorption isotherms using the BET equation. Nevertheless, a small degree of preferential water adsorption was observed on Ca- and Na-kaolin at water fractions less than 0.3, indicating that at low RH and relatively high p-xylene vapor pressure the adsorption of water was greater than could be accounted for based on single-sorbate adsorption isotherms. Water and p-xylene adsorption on Ca-, Na-, and Li-

kaolin predicted from Hill's multi-sorbate BET equation deviated, on the average, by a factor of 0.25 from the measured adsorption. These data suggest that the two-component equation of Hill (1946a, 1946b) warrants further investigation as a tool to predict the competitive adsorption of water and organic vapors at low surface coverages.

CHAPTER 5
THE EFFECT OF HEAT TREATMENTS ON THE TOTAL CHARGE AND EXCHANGEABLE CATIONS OF CA-, NA-, AND LI-SATURATED KAOLIN

Introduction

The effect of exchangeable ions on the adsorption and desorption of water vapor by kaolin has been studied in great detail (Jurinak, 1961, 1963; Jurinak and Volman, 1961a, 1961b; Keenan et al., 1951; Martin, 1959). Of particular interest is the Li ion, which has been shown to have no apparent effect on water adsorption. Martin (1959) reported that Li-saturated kaolin did not exhibit hysteresis due to cation hydration effects at relative humidities below 80%; whereas, Ca-, Mg-, and Na-saturated kaolin yielded hysteretic adsorption-desorption isotherms. In addition, kaolin saturated with Li has been found to adsorb less water than kaolin saturated with Na, despite the fact that Li has a slightly greater hydration energy than Na (Keenan et al., 1951). Based on these data, Li-saturated kaolin is generally considered to represent a mineral surface independent of cation hydration effects and has frequently been utilized as a reference surface in the study of water and organic vapor sorption on kaolin (Jurinak, 1963; Jurinak and Volman, 1961a; Rhue et al., 1989).

Although published data present strong evidence for the absence of Li hydration, the mechanisms responsible for such behavior have not been clearly

identified. Keenan et al. (1951) hypothesized that Li ions fit into the tetrahedral layer of kaolin such that hydration is sterically hindered by the outer oxygen atoms. In contrast, Martin (1959) postulated that the hydration energy of Li was not sufficient to overcome the specific adsorption energy of the ion for the clay surface, and thus true ionic hydration did not occur. In both of these studies the kaolin was dried at 70°C in a vacuum, which has been shown to be equivalent to air-drying at 115°C (Keenan et al., 1951), prior to the adsorption experiments.

The effect of heating on the cation exchange capacity (CEC) of kaolin saturated with Ca, Mg, Na, and Li was studied by Greene-Kelly (1955). Interestingly, the CEC of Li-kaolin, as determined from NH_4 exchange, was 50% of the original level after heating to 100°C. The heat treatment had no apparent effect on the CEC of Ca-, Mg-, and Na-kaolin. A reduction in NH_4 exchange by Li-kaolin after heating to 300°C was also reported by Cashen (1959). These data suggest that the reason water adsorption on Li-saturated kaolin was less than that of Na-saturated kaolin was actually due to a reduction in CEC. Jurinak (1961), Keenan et al. (1951), and Martin (1959) failed to report the CEC of kaolin following cation saturation and heat treatments, and were apparently unaware of possible charge reductions upon heating.

Greene-Kelly (1955) also reported that heating substantially decreased the the amount of Li that could be extracted from Li-kaolin using 1 N NH_4AOc. These data suggest that a portion of the Li ions were fixed within the kaolinite structure. A similar phenomenon, the migration of Li ions into the clay lattice, has

been observed for montmorillonite and is commonly referred to as the Hofmann-Klemen effect (Brindley and Ertem, 1971; Calvet and Prost, 1971; Glaser and Mering, 1971; Greene-Kelly; 1953; Hofmann and Klemen, 1950; Jaynes and Bigham, 1987; Lim and Jackson, 1986; Luca and Cardile, 1989; Luca et al., 1989; Sposito et al., 1986). Two positions have been proposed for the location of nonexchangeable Li ions in montmorillonite: (1) the bottom of the pseudohexagonal cavities of the basal surface; and (2) vacant octahedral sites. Calvet and Prost (1971), using infrared (IR) spectroscopy, found that only a fraction of the nonexchangeable Li resides within the octahedral layer, the remainder being located in the hexagonal cavities. These data were supported by Luca and Cardile (1989), who reported that Fe^{+3} migrates into the pseudohexagonal cavities, but not the vacant octahedral sites of dehydrated montmorillonite based on electron spin resonance techniques. Although there remains some controversy over the exact location of nonexchangeable Li ions, it is clear that upon heating Li migrates into the montmorillonite structure.

The purpose of this study was to determine the effect of heating on the total charge and exchangeable cations of Ca-, Na-, and Li-saturated kaolin. It was hypothesized that Li migrates into kaolin upon heating, in a manner similar to that reported for montmorillonite (i.e., the Hofmann-Klemen effect). Infrared spectroscopy was utilized to infer the location of Li ions in heat-treated kaolin. The effect of heat and vacuum treatments on the adsorption and desorption of water vapor by kaolin was also studied.

Materials and Methods

Kaolinite Samples

The kaolinite samples studied were colloidal kaolin (K-6, Lot #731063), obtained from Fisher Scientific Products, and KGa-1 kaolinite from Washington County, Georgia, obtained from the Source Clays Repository of The Clay Minerals Society. The reported CEC values for KGa-1 kaolinite range from 1.7 to 2.4 $cmol_c/kg$ (van Olphen and Fripiat, 1979). The KGa-1 kaolinite was considered to be well-crystallized, with a N_2 surface area of 10.05 ± 0.02 m^2/g. The Fisher kaolin had a slightly larger CEC (3.3 $cmol_c/kg$ at pH 4.0) and was predominantly Na-saturated with trace amounts of exchangeable Ca, Mg, and K (Rhue and Reve, 1990). Additional physical and chemical characteristics of Fisher kaolin are given in Chapter 2.

X-Ray Diffraction Studies

Due to the lack of mineralogical data for Fisher kaolin, x-ray diffraction (XRD) studies were undertaken to provide a preliminary mineralogical characterization and to determine the relative degree of order in the mineral structure. Oriented mounts of Fisher kaolin were prepared for XRD analysis by depositing approximately 300 mg of kaolin from suspension onto a ceramic tile under suction. The kaolin mounts were treated with 1 M $MgCl_2$ and KCl, and washed free of salts with deionized water. A 30% glycerol solution was applied to the Mg-saturated samples. All mounts were scanned with a computer-controlled XRD system operated at 2.0° 2Θ per minute using CuKα radiation. The XRD

analyses were performed at room temperature (≈ 24°C) and after overnight heating at 110, 300, and 550°C.

Cation Exchange Capacity Experiments

Prior to cation saturation, Fisher kaolin was treated with 1 M NaAOc buffered to pH 4.11 with acetic acid to remove carbonates. Homoionic samples of Ca-, Na-, and Li-saturated Fisher kaolin were prepared following the procedure described in Chapter 4. With the exception of the NaAOc treatment, the same procedure was followed to saturate the KGa-1 kaolin with Ca, Na, and Li.

A preliminary experiment was conducted to determine the effect of heating (130°C) on the CEC of Fisher kaolin saturated with Ca, Na, and Li. The amount of saturating cation which remained exchangeable after 0, 2, 7, and 15 days of exposure to heat was measured using a $Mg(NO_3)_2$ extraction procedure. Approximately 0.5 g of kaolin was placed in a 50 mL polyethylene centrifuge tube. To each tube 10 mL of 0.5 M $Mg(NO_3)_2$ was added, which was mixed until the kaolin was completely dispersed, and separated by centrifugation at 2500 rpm for 5 minutes. The supernatant from five $Mg(NO_3)_2$ washes was collected in a 100 mL volumetric flask, which was brought to volume with deionized water. The concentration of the appropriate cation (i.e., Ca, Na, Li) in the $Mg(NO_3)_2$ extract was measured by atomic absorption spectroscopy and expressed as $cmol_c/kg$. Aluminum was also measured in the $Mg(NO_3)_2$ extracts of Na- and Li-saturated kaolin on day 15.

After seven days of heating, the total charge of the Ca-, Na-, and Li-saturated Fisher kaolin was determined by Ca-exchange. An additional 0.5 g sample of kaolin was placed in a 50 mL polyethylene centrifuge tube. The kaolin was washed five times with 20 mL of 1 M $CaCl_2$, and excess salt was removed by repeatedly washing the kaolin with 95% ethanol until a negative chloride test was achieved using $AgNO_3$. Calcium was extracted with 0.5 M $Mg(NO_3)_2$, following the same procedure as described previously.

A second, more extensive study was initiated to determine the effect of heating at 110°C on the total charge and exchangeable cations of Ca-, Na-, and Li-saturated Fisher and KGa-1 kaolin. Approximately 0.5 g of kaolin was placed in individual 50 mL polyethylene centrifuge tubes. The samples were washed with 20 mL of 1 M NH_4Cl to extract exchangeable Ca, Na, Li, Mg, and Al. The total charge of the kaolin was then determined by Ca-exchange, as described previously. The Na- and Li-saturated kaolin samples were also treated with 0.1 M HCl for 30 minutes to extract additional Na, Li, and Al. All extractions described here were replicated four times.

Hysteresis Experiments

Thermal-gravimetric analysis (TGA) of Ca- and Li-saturated Fisher and KGa-1 kaolin was conducted to determine the effect of heating on water vapor adsorption and desorption. Approximately 15 mg of kaolin was placed in the sample pan of a computer-controlled thermal-gravimetric analyzer. The samples were equilibrated with a high RH (≈90-95%) air flow stream for 2 hours at 24°C,

heated to 150°C (at a rate of 20°C per minute) for 48 hours, and allowed to reequilibrate with the high RH flow stream at 24°C for approximately 20 hours. A second treatment sequence consisted of exposure to the high RH flow stream with the temperature alternating between 24°C and 150°C every 2 hours.

A Cahn® electrobalance was used to study the effect of exposure to a vacuum on the adsorption and desorption of water vapor by Ca- and Li-saturated Fisher kaolin. Approximately 25 mg of kaolin was placed on a hanging sample pan (loop A) which was counterbalanced by an empty hanging pan (loop C). A glass tube containing water was placed over loop A in order to expose the kaolin to water vapor. The kaolin was then allowed to equilibrate until the sample weight was constant, approximately 2 hours. The glass tube was then replaced by one containing no water and a vacuum of approximately 0.18 torr was applied to the system. The kaolin was allowed to equilibrate for approximately 8 hours, after which time the system was returned to atmospheric pressure and the empty glass tube was replaced with one containing water. The weight of kaolin was recorded by an IBM-AT compatible computer that was connected to the Cahn® microprocessor via a RS-232 cable.

Infrared Spectroscopy Experiments

Suspensions of Fisher kaolin were made by placing approximately 1.5 g of kaolin in 10 mL of deionized water. A sample from the suspension was air-dried onto a small piece of a 25 mm X 2 mm ZnSe disk. The ZnSe was positioned on a standard KBr mount in a sample compartment evacuated to 0.05 torr in order to

eliminate interferences from atmospheric CO_2 and water vapors. Infrared spectra were collected using a Bomem DA3.10 Fourier-transform IR spectrometer. The DA3.10 spectrometer was equipped with a Michelson interferometer containing a KBr beamsplitter positioned at a 30° angle to the optical axis. A mercury-cadmium-telluride (MCT) detector with a D* value of 3.13 X 10^9 $cmHz^{0.5}$ and a low frequency cutoff of 400 cm^{-1} (25 m) was used in this study. The Bomem DA3.10 spectrometer was controlled by a DEC Vaxstation-II computer via an IEEE-488 interface. An optical resolution of 2.0 wavenumbers was used for the collection of the reported IR spectra.

Results and Discussion

X-Ray Diffraction Studies

The K-saturated sample exhibited strong peaks at 0.72 and 0.36 nm, which are characteristic of 001 and 002 peaks for kaolinite (Figure 5-1). A very small peak, located at 1.42 nm, was investigated in more detail to determine if the kaolin was contaminated with smectite. Heating the sample to 110 and 300°C had no discernable effect on the 1.42 nm peak; however, all peaks were eliminated at 550°C (Figure 5-2). The Mg-saturation and glycerol treatment did not result in a shift of the 1.42 nm peak (Figure 5-3b). These data indicate that the 1.42 nm peak was not due to smectite contamination, but was probably attributable to a chlorite of low thermal stability.

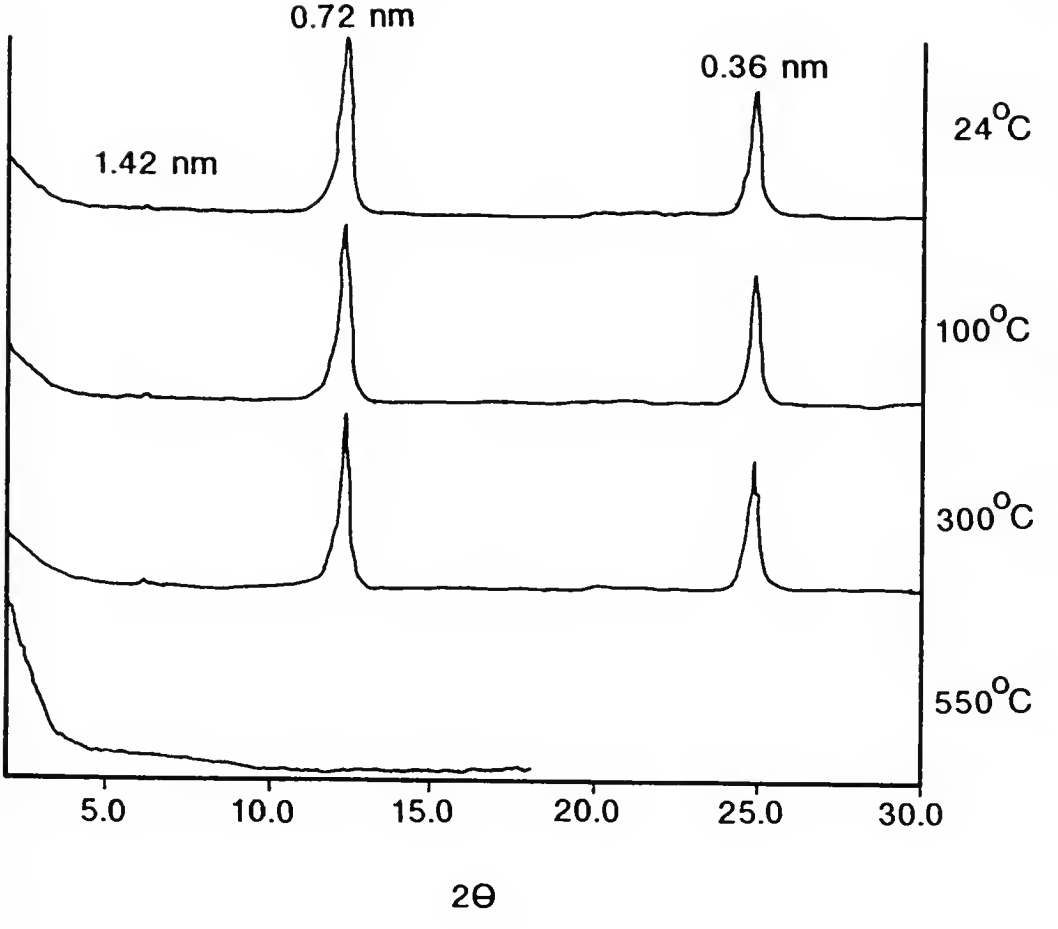

Figure 5-1. XRD patterns of K-saturated Fisher Kaolin after overnight exposure to the specified temperatures.

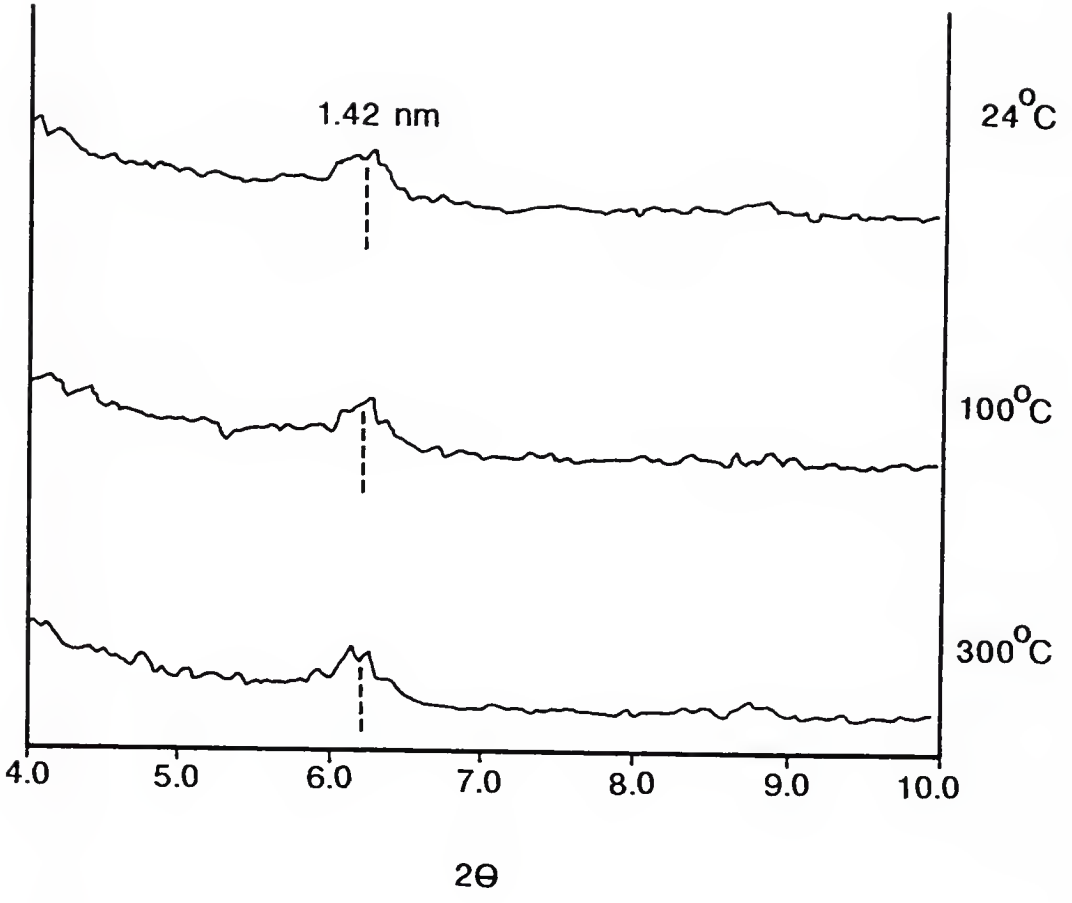

Figure 5-2. Effect of overnight exposure to the specified temperatures on the 1.42 nm peak of K-saturated Fisher kaolin.

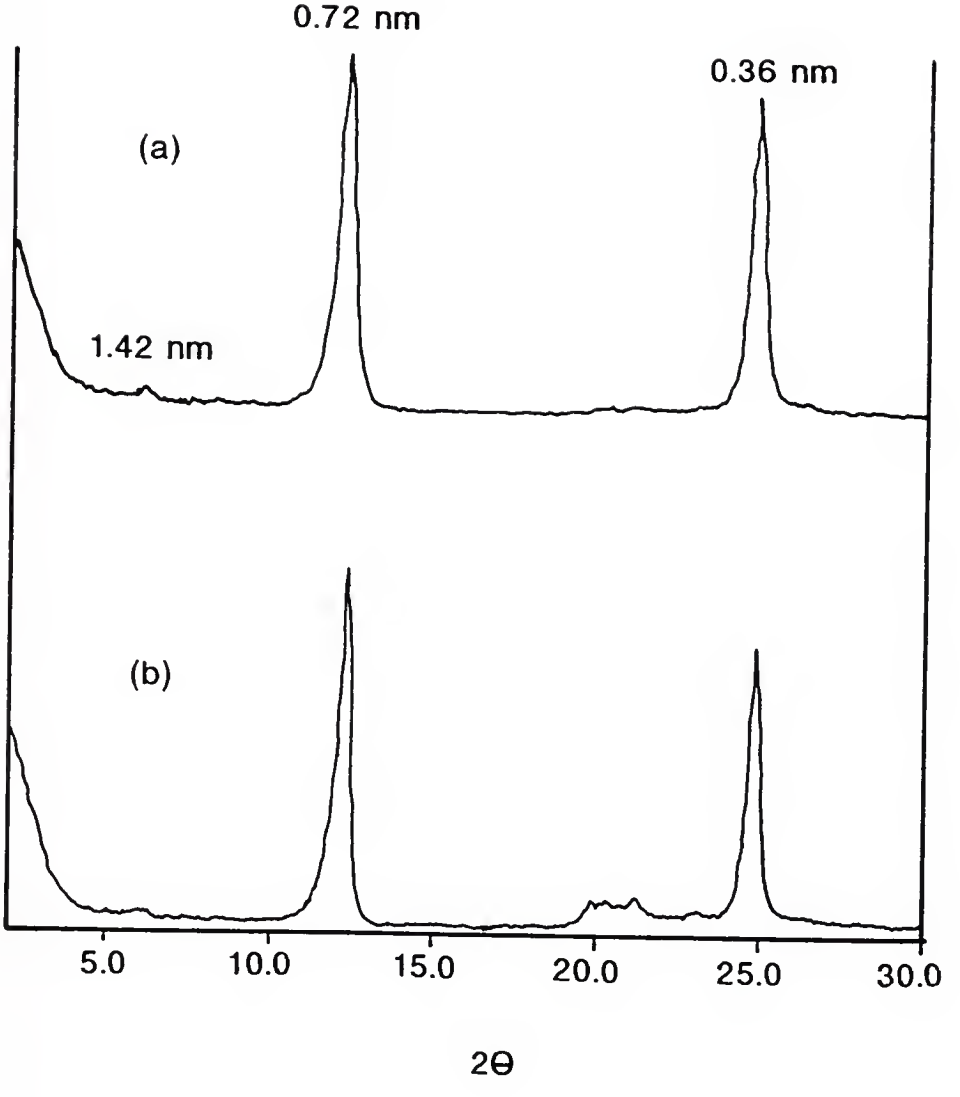

Figure 5-3. XRD pattern of Mg-saturated and glycerol treated (a) clay fraction and (b) unfractionated Fisher kaolin.

The kaolin sample was separated into silt (50-2 μm) and clay (< 2 μm) fractions to determine if the contaminant could be isolated. Separation of the kaolin was achieved by repeated dispersion, centrifugation, and collection of the supernatant. Prior to each centrifugation, pH 10 water was added to the kaolin sample. Centrifugation proceeded as follows: (1) 2000 rpm for 5 minutes, (2) 1500 rpm for 10 minutes, and (3) 1000 rpm for 2 minutes. Step 3 was repeated until the supernatant was essentially clear, after approximately five additional treatments. The supernatant collected after each centrifugation step was considered to be the clay fraction, while the residual in centrifugation tube was the silt fraction.

Oriented clay mounts of the silt and clay fractions were made following the procedure described previously. The Mg-saturation and glycerol treatment of the clay fraction yielded essentially the same peaks that were obtained for the whole clay sample (Figure 5-3a). The K-saturated silt fraction was identical to that of the whole clay, indicating that the 1.42 nm peak exists in both fractions. However, the small peak at 9.93 nm was attributed to mica (Figure 5-4). A faint peak was also observed in the whole clay sample at approximately 9.9 nm. The contamination noted here was likely to have little effect on the CEC and surface area of the kaolin because it appeared to be attributable to non-expandable phyllosilicate minerals of low surface charge.

Semi-random powder mounts of the Fisher kaolin were prepared by gently packing air-dry kaolin into the sample reservoir of a plastic mount. A powder mount allows all crystal planes (h,k,l) to be detected by XRD analysis. As the

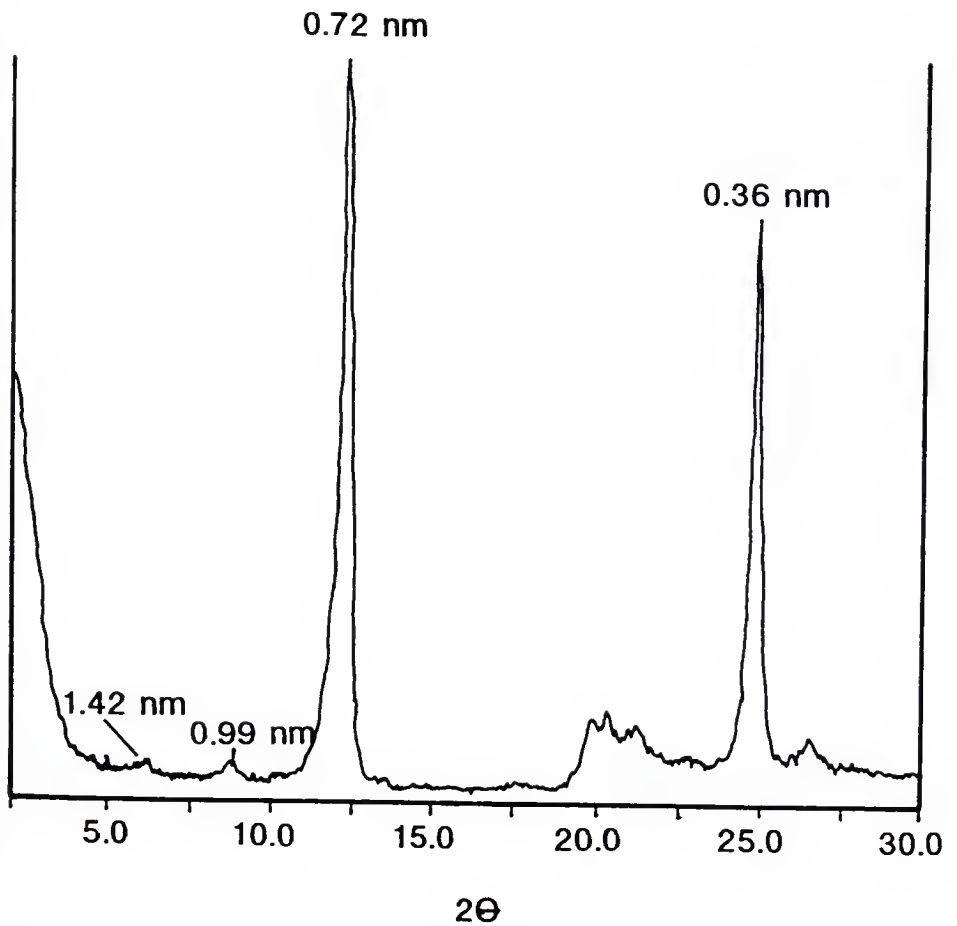

Figure 5-4. XRD pattern of K-saturated silt fraction of Fisher kaolin.

order of the kaolin decreases, the 001 peak will tend to broaden and the 020, 110, 111, 111, 021, and 021 peaks will lose resolution. A comparison of the XRD diffraction patterns of Fisher kaolin, well-crystallized Ga kaolin, and poorly-crystallized Ga kaolin are shown in Figure 5-5. The 020, 110, 111, 111, 021, and 021 peaks were clearly identifiable in the Fisher kaolin and well-crystallized kaolin, but were not readily discernable in the poorly-crystallized kaolin. These data suggest that the Fisher kaolin approached the order of the well-crystallized kaolin, and thus was considered to be medium- to well-crystallized.

Cation Exchange Capacity

The results of the preliminary CEC experiment are presented in Table 5-1. After seven days of heating at 130°C, the amount of Ca extracted from Ca-saturated Fisher kaolin had not changed, whereas extractable Na and Li was 81 and 10%, respectively, of the original level. The total charge of Ca- and Na-kaolin, as determined by Ca exchange, was not affected by the heat treatment, but decreased by approximately 50% for Li-kaolin. The disparity between the charge attributable to the saturating cation and that determined by Ca exchange for Na- and Li-kaolin suggests that other ions were involved in the exchange process. To test this hypothesis, the $Mg(NO_3)_2$ extracts of Na- and Li-kaolin were analyzed for Al on day 15. Aluminum was not detected in the Na-kaolin extract, but was present in the Li-kaolin extract, suggesting that Li displaced Al from the kaolin lattice. It should also be noted that the color of the Li-kaolin changed from nearly white to gray upon heating. The color of Ca-kaolin was not affected the heat

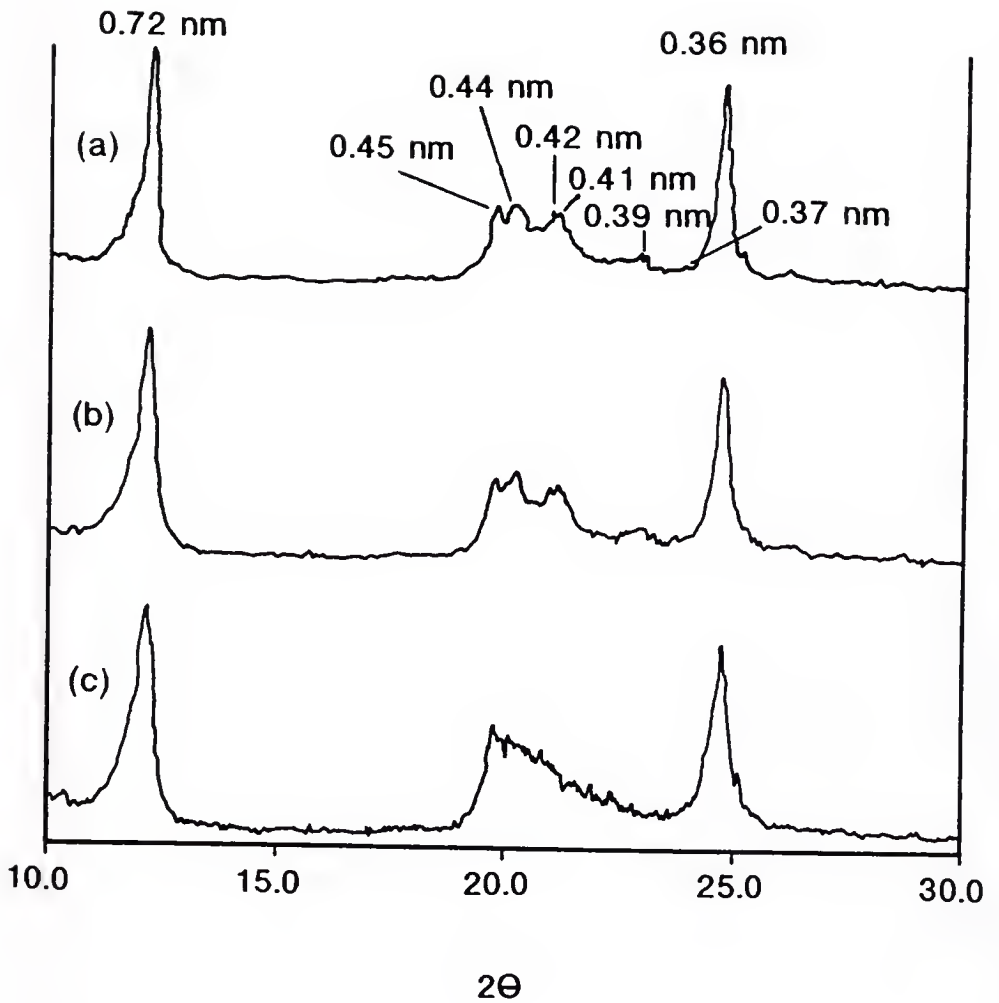

Figure 5-5. XRD patterns from powder mounts of (a) well-crystallized Ga kaolin, (b) Fisher kaolin, and (c) poorly-crystallized Ga kaolin.

Table 5-1. Results of preliminary experiment to determine the effect of heating at 130°C on the CEC of Ca-, Na-, and Li-saturated Fisher kaolin.

Elapsed Days	Extraction Method	Ca-kaolin	Na-kaolin	Li-kaolin
		----------cmol$_c$/kg----------		
0	$Mg(NO_3)_2$[a]	4.107 ± 0.005	3.547 ± 0.056	3.809 ± 0.039
2	$Mg(NO_3)_2$	3.951 ± 0.018	3.034 ± 0.057	0.598 ± 0.014
7	$Mg(NO_3)_2$	3.981 ± 0.031	2.862 ± 0.066	0.391 ± 0.027
	$CaCl_2$[b]	3.709 ± 0.032	3.523 ± 0.022	1.985 ± 0.009
15	$Mg(NO_3)_2$	-------	2.283 ± 0.022	0.209 ± 0.007
	$Mg(NO_3)_2$/Al[c]	-------	0.000 ± 0.000	0.819 ± 0.015

[a] $Mg(NO_3)_2$ extraction of saturating cation.
[b] $CaCl_2$ wash, 95% ethanol rinse, and $Mg(NO_3)_2$ extraction of Ca.
[c] $Mg(NO_3)_2$ extraction of Al.

treatment, while that of Na-kaolin became slightly darker. A similar color change has been reported for Li-saturated montmorillonite subject to heat treatments (Jaynes and Bigham, 1987).

To substantiate the findings of the preliminary experiment, a second study was conducted to determine the effect of heating on the CEC and extractable cations of kaolin. The total charge, as determined by Ca exchange, of Fisher and KGa-1 kaolin air-dried at 110°C is presented in Tables 5-2 and 5-3, respectively. After seven days of heating, the total charge of Ca-, Na-, and Li-saturated Fisher kaolin was 87, 82, and 51%, respectively, of the charge prior to heating. The KGa-1 kaolins exhibited a similar trend after 18 days of heating, although the decrease in charge of Ca- and Li-kaolin was less than that of the corresponding Fisher kaolin. The reduction in total charge or CEC of Li-kaolin was consistent with the findings of Greene-Kelly (1955) and Cashen (1959). In addition, no chloride was detected in the $Mg(NO_3)_2$ extracts, indicating that positive charge did not develop as a result of heating.

The effect of heating on the amount of Ca, Na, Li, Mg, and Al extracted from Fisher and KGa-1 kaolins is presented in Tables 5-4 and 5-5, respectively. A slight decrease in the extractable Ca was observed for Ca-kaolin, along with trace amounts of Na, Mg, and occasionally Al. In contrast, Li-kaolin exhibited a dramatic decrease in exchangeable Li upon heating, with a corresponding increase in Al. The retention of Li ions after heating has also been reported for Li-saturated Peerless No. 2, English Clays, and Merck kaolin (Greene-Kelly, 1955).

Table 5-2. Total charge of Ca-, Na-, and Li-saturated Fisher kaolin, as determined by Ca exchange, air-dried at 110°C.

Elapsed Days	Ca-kaolin	Na-kaolin Cation Exchange Capacity	Li-kaolin
	----------cmol$_c$/kg----------		
0	3.938 ± 0.050	4.272 ± 0.041	3.789 ± 0.005
2	3.597 ± 0.016	3.667 ± 0.022	2.450 ± 0.058
7	3.445 ± 0.054	3.485 ± 0.025	1.947 ± 0.019

Table 5-3. Total charge of Ca, Na, and Li-saturated KGa-1 kaolin, as determined by Ca exchange, air-dried at 110°C.

Elapsed Days	Ca-kaolin	Na-kaolin Cation Exchange Capacity	Li-kaolin
	----------cmol$_c$/kg----------		
0	2.443 ± 0.011	2.453 ± 0.032	2.149 ± 0.025
2	2.434 ± 0.009	2.306 ± 0.025	1.766 ± 0.072
8	2.075 ± 0.027	1.803 ± 0.019	1.291 ± 0.020
18	2.301 ± 0.003	1.951 ± 0.005	1.450 ± 0.029

Table 5-4. Charge attributable to Ca, Na, Li, Mg, and Al extracted from Ca-, Na-, and Li-saturated Fisher kaolin air-dried at 110°C.

Elapsed Days	Cation	Ca-kaolin	Na-kaolin	Li-kaolin
		----------cmol$_c$/kg----------		
0	Ca	3.845 ± 0.038	0.075 ± 0.002	0.010 ± 0.002
	Na	0.052 ± 0.010	3.671 ± 0.039	0.062 ± 0.004
	Li	------	------	3.597 ± 0.023
	Al	0.000 ± ------	0.000 ± ------	0.000 ± ------
	Mg	0.025 ± 0.001	0.031 ± 0.001	0.024 ± 0.001
2	Ca	3.684 ± 0.023	0.048 ± 0.000	0.000 ± ------
	Na	0.110 ± 0.002	3.013 ± 0.037	0.114 ± 0.006
	Li	------	------	1.163 ± 0.076
	Al	0.097 ± 0.034	0.164 ± 0.039	0.601 ± 0.024
	Mg	0.027 ± 0.002	0.029 ± 0.002	0.020 ± 0.001
7	Ca	3.623 ± 0.018	0.053 ± 0.005	0.000 ± ------
	Na	0.157 ± 0.006	2.828 ± 0.031	0.153 ± 0.002
	Li	------	------	0.315 ± 0.004
	Al	0.102 ± 0.007	0.142 ± 0.010	0.977 ± 0.085
	Mg	0.025 ± 0.001	0.027 ± 0.000	0.011 ± 0.001
15	Ca	3.512 ± 0.018	0.044 ± 0.009	0.000 ± ------
	Na	0.173 ± 0.002	2.737 ± 0.022	0.195 ± 0.015
	Li	------	------	0.245 ± 0.007
	Al	0.000 ± ------	0.157 ± 0.056	1.198 ± 0.066
	Mg	0.030 ± 0.001	0.020 ± 0.000	0.004 ± 0.002
40	Ca	3.554 ± 0.015	0.039 ± 0.003	0.000 ± ------
	Na	0.191 ± 0.003	2.624 ± 0.058	0.183 ± 0.006
	Li	------	------	0.205 ± 0.005
	Al	0.000 ± ------	0.187 ± 0.032	0.905 ± 0.019
	Mg	0.026 ± 0.003	0.022 ± 0.001	0.007 ± 0.004

Table 5-5. Charge attributable to Ca, Na, Li, Mg, and Al extracted from Ca-, Na-, and Li-saturated KGa-1 kaolin air-dried at 110°C.

Elapsed Days	NH_4Cl Extract	Ca-kaolin	Na-kaolin	Li-kaolin
		----------$cmol_c/kg$----------		
0	Ca	2.199 ± 0.012	0.000 ± ------	0.000 ± ------
	Na	0.044 ± 0.007	2.000 ± 0.022	0.047 ± 0.004
	Li	------	------	1.719 ± 0.014
	Al	0.000 ± ------	0.000 ± ------	0.000 ± ------
	Mg	0.043 ± 0.001	0.019 ± 0.002	0.011 ± 0.002
2	Ca	2.164 ± 0.012	0.000 ± ------	0.000 ± ------
	Na	0.124 ± 0.007	1.522 ± 0.035	0.131 ± 0.006
	Li	------	------	0.417 ± 0.012
	Al	0.064 ± 0.038	0.144 ± 0.013	0.460 ± 0.044
	Mg	0.045 ± 0.001	0.028 ± 0.001	0.025 ± 0.003
8	Ca	2.038 ± 0.021	0.000 ± ------	0.000 ± ------
	Na	0.151 ± 0.003	1.324 ± 0.023	0.147 ± 0.003
	Li	------	------	0.125 ± 0.001
	Al	0.000 ± ------	0.067 ± 0.067	0.569 ± 0.019
	Mg	0.031 ± 0.001	0.023 ± 0.008	0.013 ± 0.001
18	Ca	2.101 ± 0.014	0.000 ± ------	0.000 ± ------
	Na	0.149 ± 0.004	1.334 ± 0.017	0.152 ± 0.007
	Li	------	------	0.113 ± 0.005
	Al	0.085 ± 0.056	0.092 ± 0.031	0.524 ± 0.049
	Mg	0.038 ± 0.002	0.024 ± 0.001	0.023 ± 0.003

A similar trend was observed for Na-kaolin, but to a much lesser degree than that of Li-kaolin. It should be noted that the Fisher and KGa-1 kaolin exhibited an almost identical decrease in the percentage of Li ions extracted with 1 M NH_4Cl. However, the initial reduction (day 2) in extractable Li was less than that measured at 130°C, which suggests that temperature influenced the rate of Li retention. The data presented here clearly demonstrate that heating Li-saturated kaolin results in Li retention and a decrease in total charge or CEC.

The sum of charge attributable to Ca, Na, Mg, and Al extracted from Ca-saturated Fisher and KGa-1 kaolin remained essentially constant over the treatment periods (Figures 5-6a and 5-7a). These data were in agreement with the total charge measured by Ca-exchange. In contrast, the sum of cation charges for Na-kaolin decreased slightly, while that of Li-kaolin decreased substantially as a result of heating. Figures 5-6c and 5-7c clearly indicate that exchangeable Al contributed significantly to the charge of Li-kaolin after heating, and suggest that a portion of the Li retained by the kaolin displaced Al from the clay lattice. These data are contrary to those reported by Greene-Kelly (1955), who extracted only trace amounts of Al from Li-kaolin before and after heating, using a 0.001 M HCl and 1 M NH_4Cl extraction procedure. However, Greene-Kelly (1955) apparently washed the kaolin with 1 M NH_4AOc (pH 7) prior to extracting Li ions. This treatment may have precipitated exchangeable Al, which was then not extractable with the weak acid and NH_4Cl.

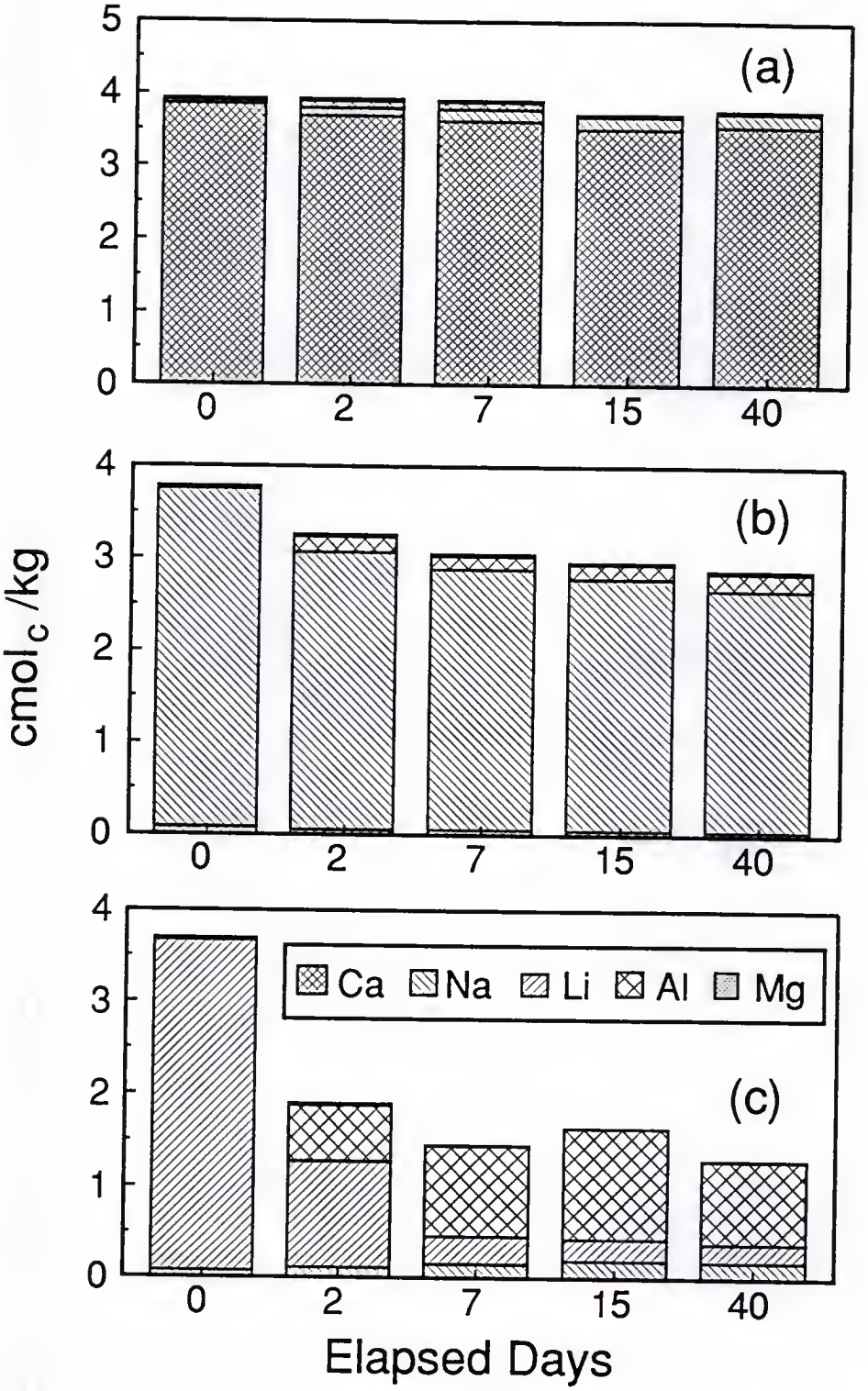

Figure 5-6. The sum of Ca, Na, Li, Mg, and Al extracted from (a) Ca-, (b) Na-, and (c) Li-saturated Fisher kaolin.

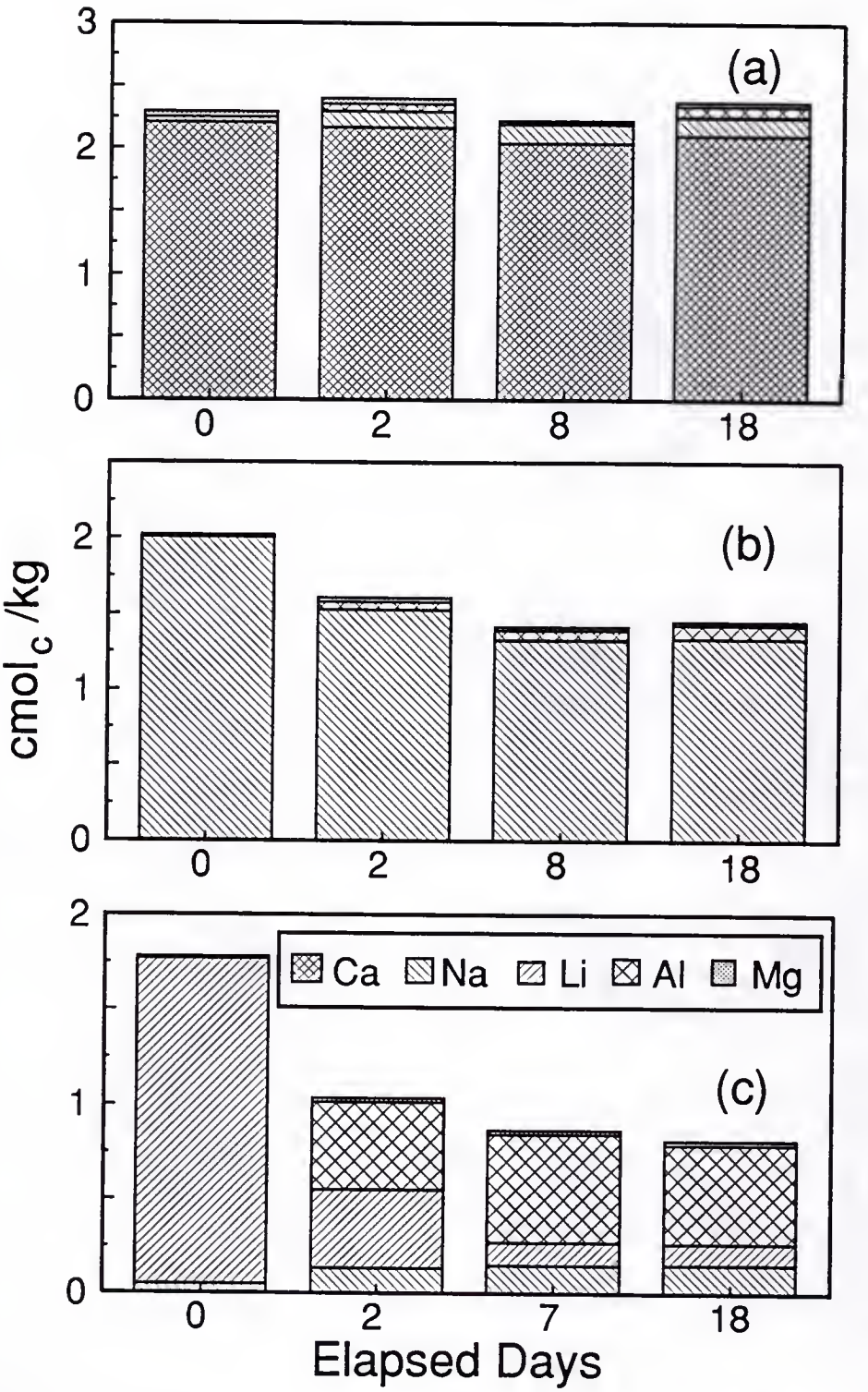

Figure 5-7. Sum of Ca, Na, Li, Mg, and Al extracted from (a) Ca-, (b) Na-, and (c) Li-saturated KGa-1 kaolin.

Even though Al contributed to the charge of Na- and Li- kaolin, a considerable difference remained between the total charge determined by Ca exchange and that determined from the sum of extractable Ca, Na, Li, Mg, and Al. This discrepancy suggests that other cations contributed to the total charge of the kaolin. Interestingly, Cashen (1958) reported that heated samples of Na- and Li-saturated Peerless No. 2 kaolin were far more acid than untreated samples. Thus, the heating of Li-kaolin and subsequent retention of Li ions may also have caused the displacement of H ions from the clay lattice. This hypothesis is supported by Farmer and Russell (1967), who proposed that a portion of the Li ions that migrate into montmorillonite react with interlayer water or structural hydroxyls to liberate protons. Although the inclusion of H ions may bring the charge determined from the sum of extractable cations into agreement with the value obtained by Ca-exchange, the fact remains that the heat treatment reduced the total charge of Na- and Li-kaolin.

In an attempt to extract non-exchangeable Na and Li from the heat-treated Fisher kaolin, the kaolin was washed with 0.1 M HCl for successive 15 minute intervals. However, only a small amount of Li and trace levels of Na were recovered (Table 5-6). A total elemental analysis of the heat-treated kaolin would be likely to recover all the retained Li; however, the exact quantity of Li involved in charge reduction would still be difficult to ascertain. After the original heat treatment, Greene-Kelly (1955) reported that Peerless kaolin was capable of fixing an additional 11 $cmol_c/kg$ of Li, after nine LiCl washes and heat treatments, with

Table 5-6. Amount of Li, Na, and Al extracted from Na- and Li-saturated Fisher kaolin air-dried at 110°C using 0.1 M HCl.

Elapsed Days	HCl Trt.	Na Kaolin		Li Kaolin	
		Na	Al	Li	Al
	-min.-	----------cmol$_c$/kg----------			
0	15	------	------	0.000 ± ------	1.040 ± 0.009
	30	------	------	0.000 ± ------	0.295 ± 0.011
2	15	0.011 ± 0.001	1.577 ± 0.022	0.007 ± 0.000	0.995 ± 0.051
	30	0.005 ± 0.000	0.443 ± 0.014	0.000 ± ------	0.478 ± 0.045
7	15	0.014 ± 0.001	1.519 ± 0.013	0.025 ± 0.002	1.169 ± 0.020
	30	0.002 ± 0.000	0.699 ± 0.021	0.008 ± 0.001	0.721 ± 0.062
15	15	0.014 ± 0.013	1.531 ± 0.443	0.019 ± 0.001	1.046 ± 0.026
	30	0.001 ± 0.001	0.395 ± 0.021	0.006 ± 0.002	0.356 ± 0.012
40	15	0.000 ± ------	1.758 ± 0.049	0.042 ± 0.062	1.344 ± 0.042
	30	0.000 ± ------	0.356 ± 0.016	0.010 ± 0.001	0.345 ± 0.024

a further reduction in total charge of only 0.5 $cmol_c/kg$. These data, although somewhat puzzling at first, suggest that only a portion of the retained Li was actually involved in charge reduction, while the remainder displaced Al and H ions, which were then exchangeable.

Adsorption and Desorption of Water Vapor

The adsorption and desorption of water following heating of Ca- and Li-saturated Fisher kaolin, measured by TGA, are presented in Figures 5-8, 5-9, and 5-10. Figures 5-8 and 5-9 are representative of the weight change recorded for kaolin samples exposed to an air flow stream at ≈90-95% RH, subject to the following sequence of heat treatments: (1) room temperature for two hours, (2) 150°C for 48 hours, and (3) room temperature for approximately 24 hours. The Ca- and Li-kaolin regained an average of 98.9 ± 1.8% and 46.3 ± 1.3%, respectively, of their original weight lost due to the 150°C heat treatment. The degree of hysteresis exhibited by Li-kaolin was consistent with the 50% reduction in the total charge measured for Li-kaolin after seven days at 110 and 130°C, and after long-term exposure to heat as reported in Chapter 4. The absence of hysteresis observed for Ca-kaolin was in agreement with the stability of the total charge of Ca-kaolin upon heating. The KGa-1 kaolin also exhibited hysteresis. Ca- and Li-saturated KGa-1 kaolin regained 84.8 ± 5.2% and 57 ± 5.0%, respectively, of the original weight lost after heating. The total charge reduction of Ca- and Li-kaolin was 94 and 67%, respectively, of the level prior to heating. This discrepancy may have been due to particle coalescence of the well-crystallized KGa-1 kaolin during heat treatments. However, the overall similarity

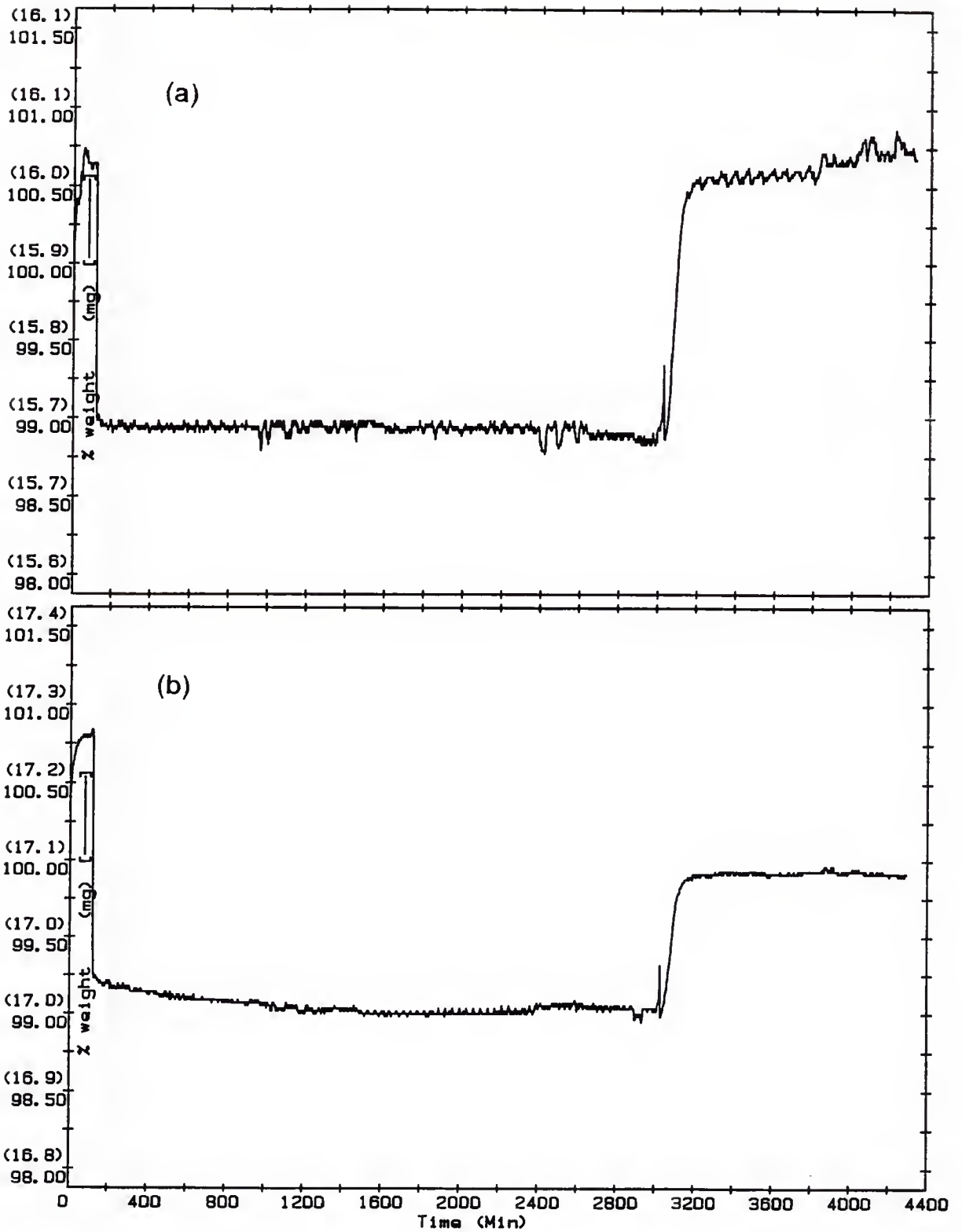

Figure 5-8. Adsorption and desorption of water by (a) Ca-saturated, and (b) Li-saturated Fisher kaolin measured by TGA.

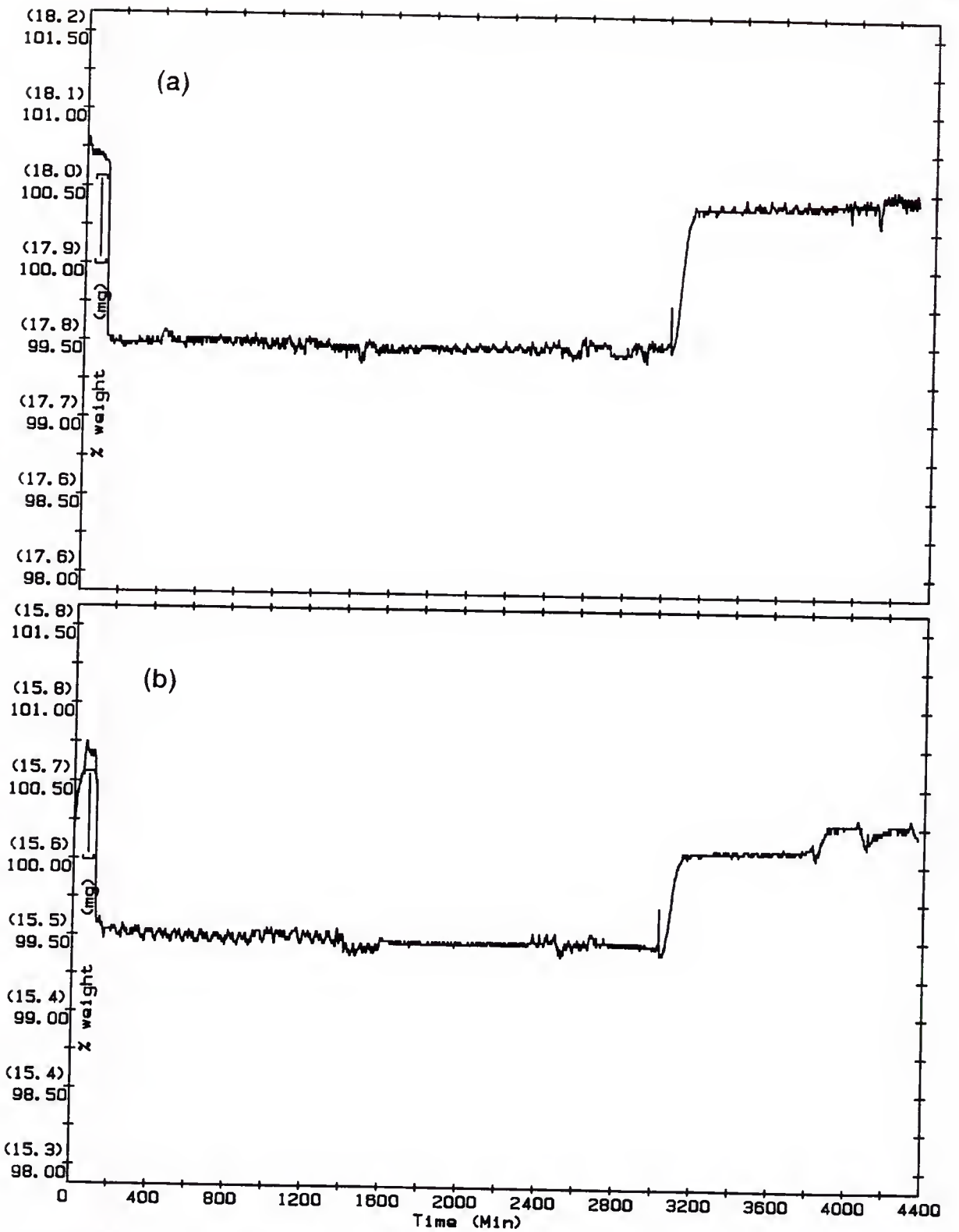

Figure 5-9. Adsorption and desorption of water by (a) Ca-saturated, and (b) Li-saturated KGa-1 kaolin measured by TGA.

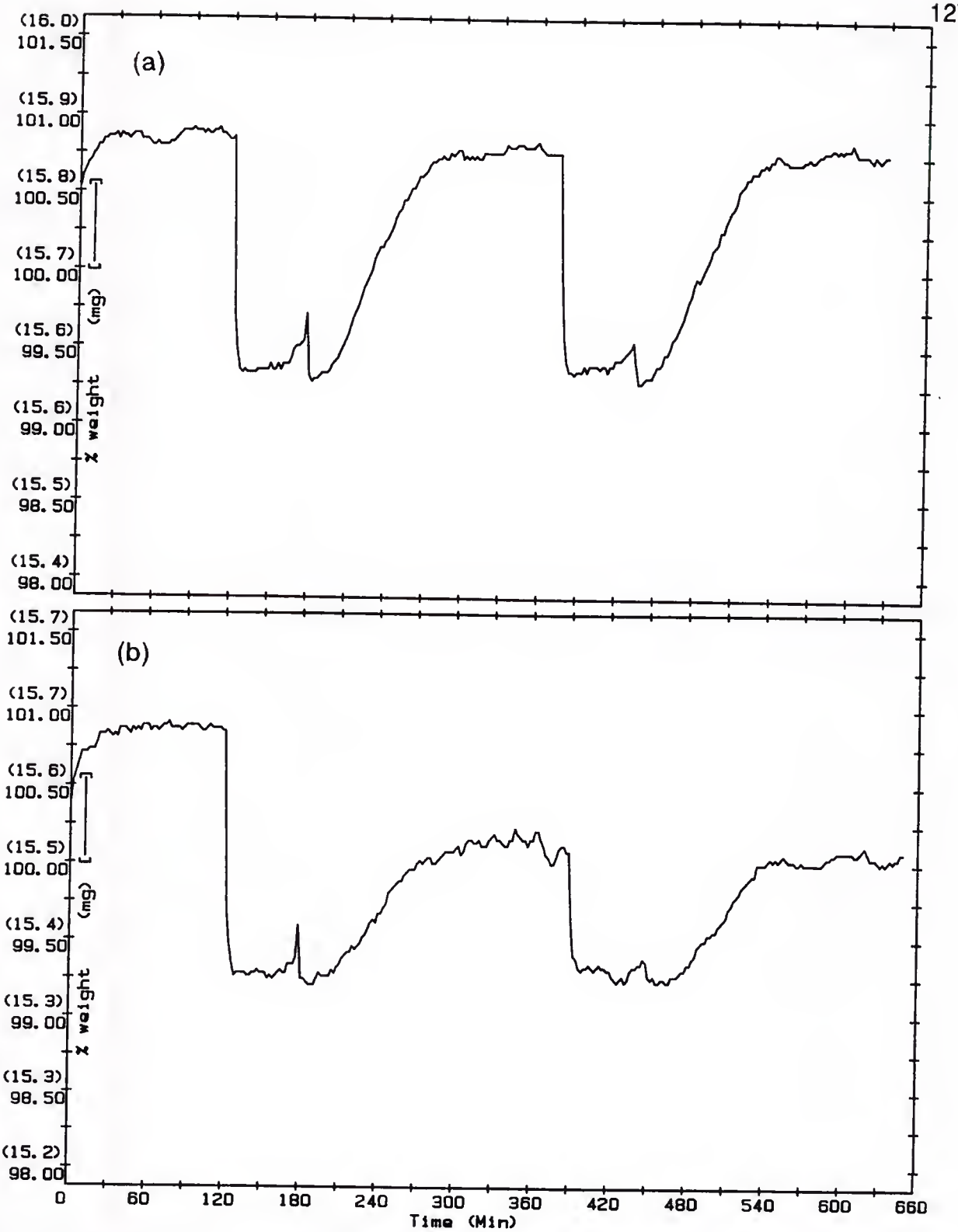

Figure 5-10. Adsorption and desorption of water by (a) Ca-saturated and (b) Li-saturated Fisher kaolin exposed to repeated 150°C treatments.

between the magnitude of hysteresis and reduction in total charge of kaolin upon heating suggests that reducted water adsorption observed for Li-kaolin was simply due to the reduction in the total charge or CEC of the Li-kaolin.

The percentage of weight regained by Li- (55.5 ± 3.5%) and Ca-saturated (97 ± 2.5%) Fisher kaolin subject to temperatures of 24 and 150°C for alternating two hour intervals was essentially the same as that measured after 48 hours at 150°C (Figure 5-10). These data indicate that the 2 hour treatment at 150°C was sufficient to reduce water adsorption to the extent of charge reduction observed after 7 days at 110 and 130°C. This finding was consistent with the increased rate of Li retention observed at 130°C versus 110°C, and indicates that temperature influenced the rate of Li retention and CEC reduction.

Similar experiments were conducted to determine if exposure to a vacuum would induce hysteresis by Li-saturated Fisher kaolin. After equilibration in a high RH atmosphere, Ca- and Li-kaolin regained 67 ± 6.0 % and 54 ± 1.0% of the weight lost following exposure to the vacuum (Figure 5-11). The considerable hysteresis observed for Ca-kaolin suggests that the actual effect of the vacuum on water adsorption by Li-kaolin was minimal. It is quite plausible that the vacuum resulted in considerable particle coalescence. Thus, even though the results of these experiments suggest the vacuum treatment induced a slight reduction in the water adsorption capacity of Li-kaolin, the utility of such a technique is limited by coincidental hysteresis effects.

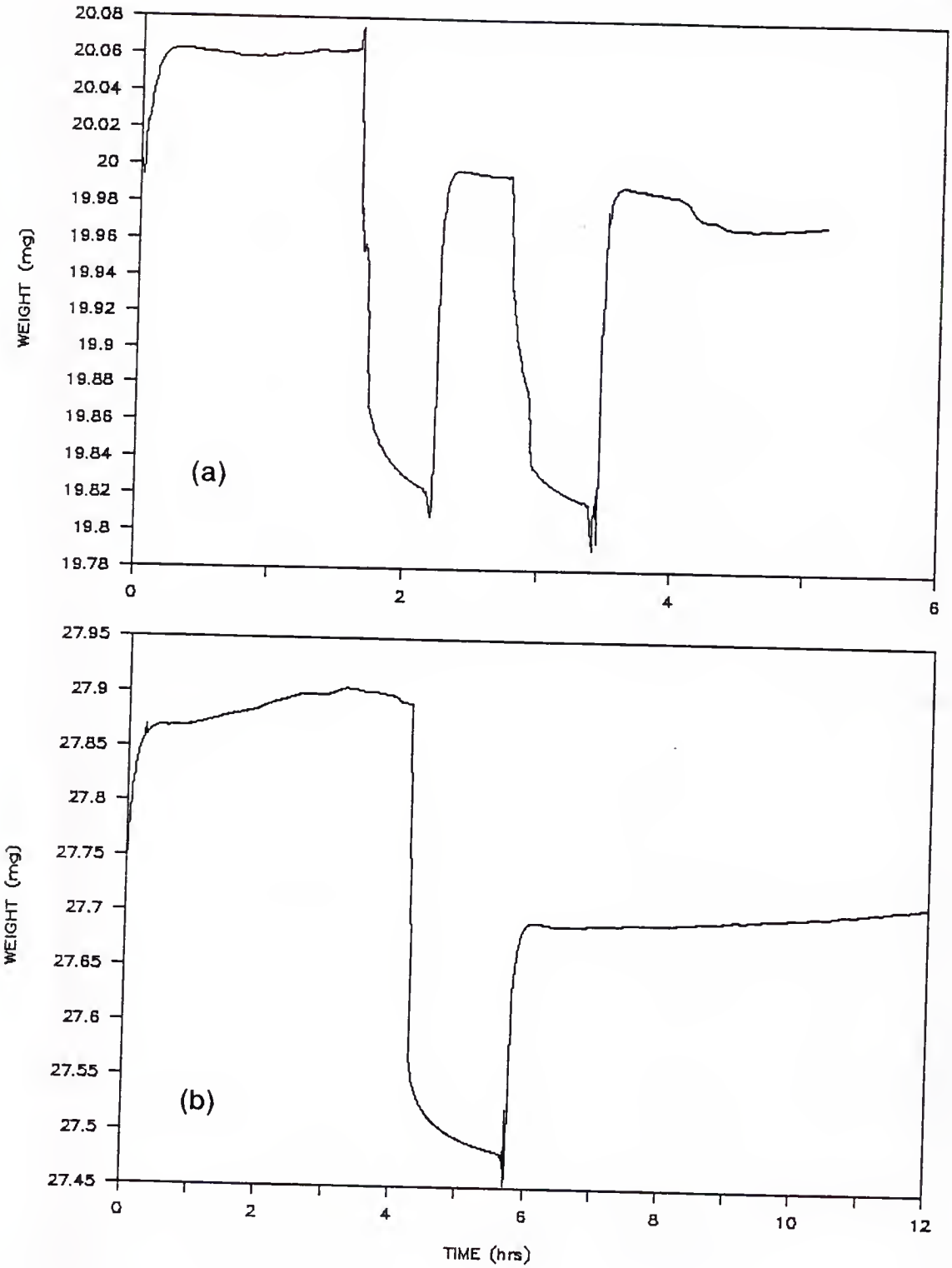

Figure 5-11. Adsorption and desorption of water by (a) Ca-saturated, and (b) Li-saturated Fisher kaolin exposed to a vacuum.

Location of Nonexchangable Li

The location of exchangeable cations on kaolin is considered to be limited to the basal plane of the tetrahedral layer; in response to permanent charge arising from the substitution of Al^{+3} for Si^{+4} in the outer tetrahedral sheet (Bolland et al., 1976; Follet, 1965; Weiss and Russow, 1963) (Figure 5-12). However, a portion of the negative charge may still be the result of pH dependent charges. Reduced water adsorption on Li-kaolin led Keenan et al. (1951) to propose that Li occupied a position in the tetrahedral layer from which hydration was sterically hindered by outer oxygen atoms. However, other cations, although small enough to fit between oxygen atoms of the tetrahedral layer, were readily hydrated. Greene-Kelly (1955), aware of the fact that Li retention and CEC reductions occurred after heating Li-kaolin, proposed that Li ions migrate into vacant octahedral coordination sites, as has been suggested to explain a similar phenomenon in montmorillonite. This hypothesis would more readily explain the displacement of Al and H from the octahedral layer. The inner hydroxyls of kaolin, which are oriented toward the octahedral cavity, yield an IR spectra band at 3620 cm^{-1}. It was hypothesized that the migration of Li into the vacant octahedral site would alter the orientation of inner hydroxyls, resulting in a shift in the 3620 cm^{-1} band or the creation of several unresolved bands.

The IR spectra obtained from air-dry Na- and Li-kaolin, and heated-treated Li-kaolin are shown in Figure 5-13. A subtraction procedure indicated that the inner hydroxyl stretching band of Na-kaolin and heat-treated Li-kaolin were not the

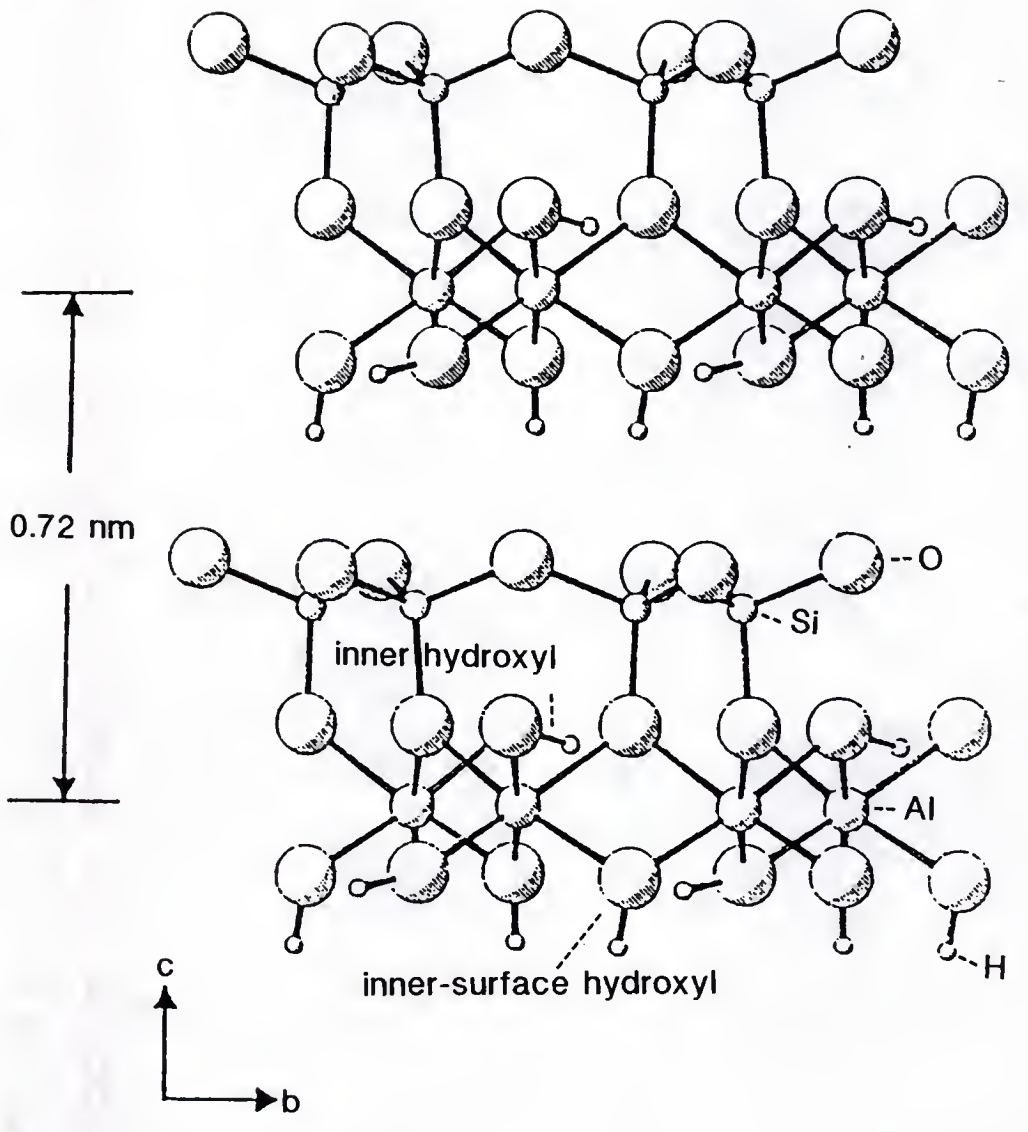

Figure 5-12. Projection of kaolinite structure onto the 100 plane.

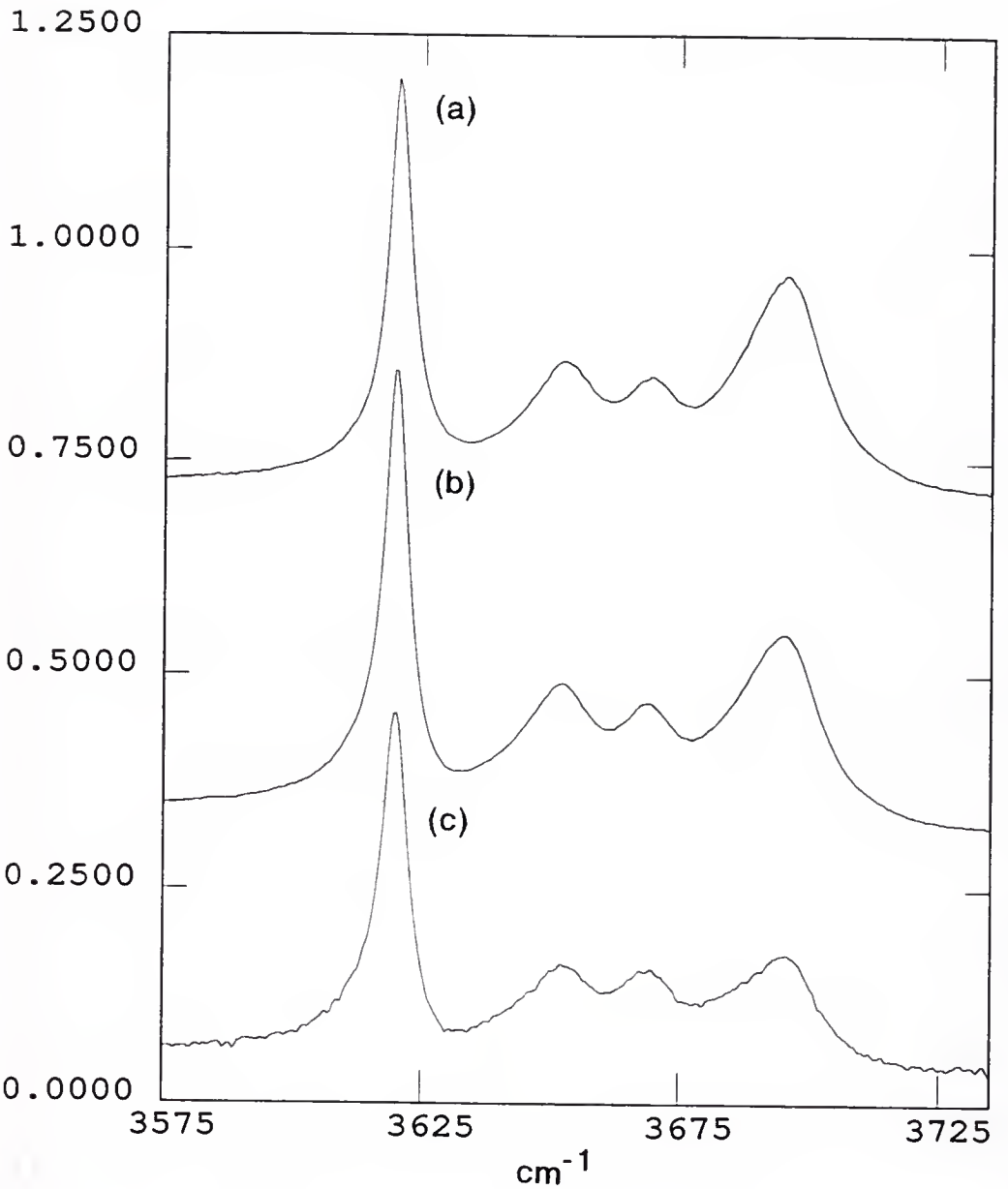

Figure 5-13. IR spectra of (a) heated Na-saturated, (b) heated Li-saturated, and (c) air-dried Li-saturated Fisher kaolin in the inner hydroxyl stretching region.

same. To substantiate this finding a deconvolution program was used to quantitatively determine the position, width, and intensity of each band (Johnston et al., 1985). Air-dry Na-kaolin yielded a single peak at 3620 cm^{-1}, whereas heat-treated Li-kaolin exhibited peaks at 3615 and 3620 cm^{-1}. The existance of a second peak at a lower wave number suggests that Li displaced a portion of the Al from the kaolin structure upon heating (C. T. Johnston, 1990, personal communication). This finding was consistent with the displacement of Al measured by ion extraction, and indicated that Li migration into the kaolin structure was directly responsible for the reduced charge of heat-treated Li-kaolin.

Summary

In a number of vapor-phase adsorption studies Li-saturated kaolin has been utilized as a reference mineral surface; considered to be independent of cation hydration effects. However, the data presented here indicate that the heating of Li-kaolin, and to a lesser extent Na-kaolin, results in a decrease in the total charge or CEC of kaolin. This effect was manifested in measurements of water adsorption following heating, which were directly related the magnitude of CEC reduction determined by Ca-exchange. These findings suggest that reduced water adsorption observed for Li-kaolin in previous studies was actually the result of a decrease in the CEC of heated Li-kaolin samples. Therefore, heat-treated Li-kaolin represents a surface of reduced charge, rather than a surface free of cation hydration effects.

Extraction of Li-kaolin with NH_4Cl revealed that only 6% of the Li ions remained exchangeable after heat treatment. A considerable amount of Al was extracted from the Li-kaolin, and yet the sum of Al, Li, Mg, Na, and Ca accounted for only 75% of the reduced CEC. Based on previous reports of increased acidity following heating, it appears likely that H contributed to the residual charge. Thus, the remaining exchange capacity of the heated Li-kaolin was satisfied by Li, Al, and possibly H.

The Li ions rendered nonexchangeable by heating apparently acted to (1) to reduce the total charge, and (2) to displace Al and H from the clay lattice. The fact that an additional 11 $cmol_c/kg$ of Li could be introduced to kaolin with only a 0.5 $cmol_c/kg$ reduction in total charge, suggests that the magnitude of total charge reduction is fixed or limited, whereas, a considerable quantity of Al and H can be displaced from the lattice. the location of Li ions could not be definitively ascertained by IR spectroscopy. These data demonstrate that heat-treated Li-kaolin cannot be treated as a reference surface, In particular, the assumption that Li-kaolin is free of cation hydration effects may lead to erroneous estimates of the number of water molecules associated with each exchangeable cation (e.g., Keenan et al., 1951).

CHAPTER 6
SUMMARY AND CONCLUSIONS

Antecedent moisture content or relative humidity (RH) is arguably the most important factor influencing vapor-phase sorption in the unsaturated zone. In Chapter 2, the effect of RH on the sorption of p-xylene vapors in the unsaturated zone was investigated at a mechanistic level. Soils and clay minerals exhibited a sizable capacity to adsorb organic vapors at low RH which was characterized by Type-II adsorption isotherms. When the RH was increased to 67 and 90%, p-xylene sorption decreased dramatically and isotherms shifted from Type-II to Type-III regardless of the organic carbon (OC) content. Increased sorption at relative vapor pressures above 0.6 has not been reported previously, and indicates that hydrated soils may adsorb significant quantities of organic vapors near the contaminant source.

The adsorption of p-xylene vapors on anhydrous sorbents was strongly correlated to mineral surface area determined from N_2 adsorption isotherms. In contrast, greater sorption was observed for untreated than hydrogen peroxide treated Webster soil at 90% RH. These data suggest that soil organic matter functions as a partitioning medium for organic vapors following hydration. In addition, the use of K_{oc} values to predict vapor-phase sorption at high RH was only applicable to sorbents of high OC content at p-xylene relative vapors less than 0.5.

Predictions of the surface excess based on the Gibbs adsorption equation suggest that adsorption at the gas-liquid interface was the dominant mechanism responsible for p-xylene sorption on kaolin and silica gel.

Vapor-phase sorption was also studied by gas chromatography, which offers an efficient and versatile alternative to conventional batch techniques (Chapter 3). Data for the sorption of p-xylene, obtained by the eluted-pulse method, on anhydrous and hydrated Oldsmar sand conformed to Type-II and Type-III isotherms, respectively. The salt treatment of Oldsmar soil resulted in decreased p-xylene sorption, which was consistent with sorption data obtained for Webster soil. At high RH, this phenomenon was attributed to a reduction in sorptive capacity at the gas-liquid interface of salt-treated soils. However, predictions of the surface excess failed to support this hypothesis, even though salt solutions exhibited a significantly greater surface tension than deionized water. Regardless of the mechanism, these data suggest that vapor-phase sorption of volatile organic chemicals (VOCs) will be significantly reduced in salt-affected soils.

In Chapter 4, the adsorption of water and p-xylene vapors on Ca-, Na-, and Li-saturated kaolin was investigated for single and mixed-vapor systems. The amount of water adsorbed on Ca- and Na-kaolin was directly related to the hydration energy of the cation. In contrast, Li-kaolin exhibited less adsorption than Na-kaolin even though the hydration energy of Li is slightly greater than that of Na. A similar effect was observed for p-xylene vapors, which suggests that weak interactions occurred between exchangeable cations and p-xylene molecules.

When the RH was increased to 10 and 20%, p-xylene adsorption decreased successively. Enhanced water adsorption exhibited at high p-xylene relative vapor pressures was attributed to cation hydration effects. In addition, the competitive adsorption of water and p-xylene was well predicted by the two-component model of Hill (1946a, 1946b).

Reduced water adsorption on Li-kaolin has been attributed to the lack of Li hydration due to steric hindrance effects (Keenan et al., 1951). However, measurements of cation exchange capacity (CEC) indicated that the total charge of Li-kaolin was reduced by 50% after heating to 120°C. The reduction in CEC and water adsorption for Li-kaolin was confirmed by extraction techniques and gravimetric analysis in Chapter 5. Extractions with NH_4Cl revealed that only 6% of the Li remained exchangeable after heating; whereas, Al and H were released from the kaolin. Thus, non-exchangeable Li ions not only reduced the total charge on kaolin but also displaced Al and H from the clay lattice. Although the location of non-exchangeable Li was not ascertained by infrared spectroscopy, it appears that Li acted as a weak acid to dissolve the clay structure. These data clearly demonstrate that heated Li-kaolin represents a surface of reduced charge, rather than a surface free of cation hydration effects. Therefore, it is recommended that Li-kaolin not be used as a reference for the study of vapor-phase sorption, and conclusions based on such an assumption appear to have no theoretical basis.

The effect of RH on vapor-phase sorption of VOCs by soil materials is summarized in Figure 6-1. In order to account for the dramatic change in sorptive capacity as a function of RH, it is recommended that vapor-phase sorption be described by a multi-mechanistic approach which includes (1) adsorption on exposed mineral surfaces, (2) partitioning into organic carbon, (3) dissolution into adsorbed water films and, (4) adsorption at the gas-liquid interface. The original BET equation and two-component BET equation of Hill (1946a, b) provided accurate predictions of p-xylene adsorption under anhydrous and low RH conditions, respectively. At RHs above which the sorbate surface is covered by at least a monomolecular layer of water, sorption may result from dissolution into adsorbed water films, partitioning into OC, and adsorption at the gas-liquid interface. The importance of each mechanism will be governed by sorbate properties, such as solubility and hydrophobicity, and sorbent properties, such as OC content.

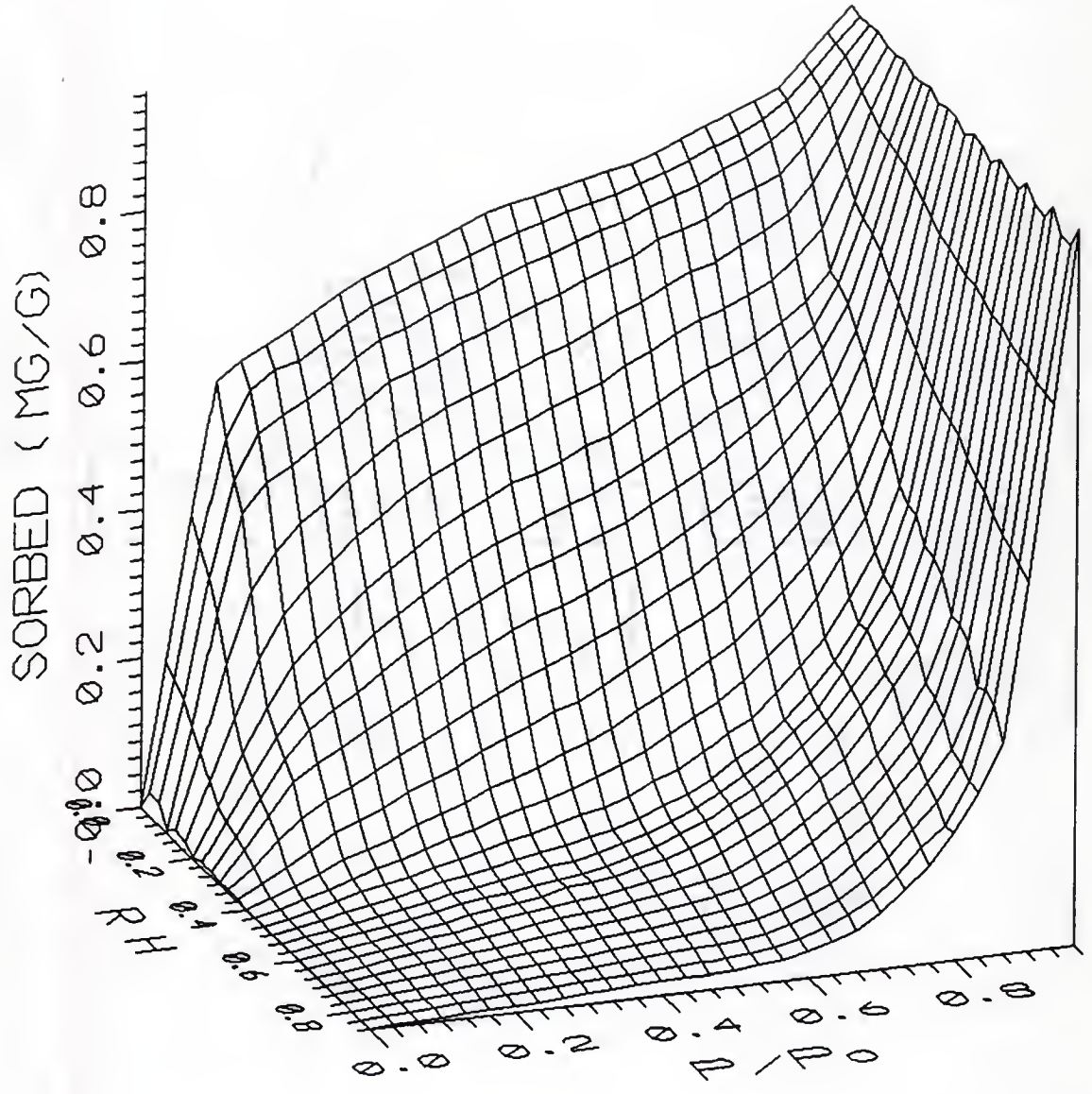

Figure 6-1. The effect of relative humidity on vapor-phase sorption by soils and clay minerals.

APPENDIX A
WATER AND P-XYLENE SORPTION DATA

Table A-1. Sorption of water and p-xylene vapors on Webster soil from single and mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			----------mg/g----------	
p-xylene	0.061 (±0.003)		4.63 (±0.15)	
	0.264 (±0.001)		7.37 (±0.05)	
	0.441 (±0.005)		9.01 (±0.00)	
+ $CaCl_2$	0.441 (±0.005)		3.03 (±0.10)	
p-xylene and water	0.099 (±0.001)	0.886 (--------)	0.21 (±0.00)	115.50 (±1.61)
	0.197 (±0.002)	0.890 (--------)	0.26 (±0.01)	93.31 (±1.70)
	0.206 (±0.000)	0.897 (--------)	0.25 (±0.01)	99.91 (±1.68)
	0.384 (±0.005)	0.899 (--------)	0.61 (±0.01)	86.68 (±1.49)
	0.497 (±0.000)	0.889 (--------)	0.63 (±0.00)	102.38 (±0.60)
	0.610 (±0.002)	0.890 (--------)	1.35 (±0.03)	86.91 (±0.11)
	0.610 (±0.002)	0.890 (--------)	1.21 (±0.01)	89.34 (±0.40)
	0.610 (±0.002)	0.890 (--------)	1.37 (±0.05)	87.63(±0.87)
	0.777 (±0.000)	0.900 (--------)	4.36 (±0.06)	87.07(±0.15)
+ $CaCl_2$	0.610 (±0.002)	0.890 (--------)	0.62 (±0.01)	116.52 (±1.84)

Table A-2. Sorption of water and p-xylene vapors on Webster HP from single and mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			----------mg/g----------	
p-xylene	0.061 (±0.003)		10.80 (±0.06)	
	0.262 (±0.002)		16.01 (±0.18)	
	0.459 (±0.006)		18.79 (±0.17)	
+ $CaCl_2$	0.459(±0.006)		11.83(±0.15)	
p-xylene and water	0.099 (±0.001)	0.886 (--------)	0.05 (±0.00)	96.19 (±1.20)
	0.201 (±0.001)	0.917 (--------)	0.08 (±0.01)	109.34 (±1.35)
	0.206 (±0.000)	0.897 (--------)	0.10 (±0.01)	89.02 (±0.72)
	0.497 (±0.000)	0.889 (--------)	0.28 (±0.01)	91.80 (±0.85)
	0.610(±0.002)	0.890 (--------)	0.91 (±0.04)	79.51 (±0.22)
	0.777(±0.000)	0.900 (--------)	3.88 (±0.12)	79.28 (±1.42)
+ $CaCl_2$	0.610 (±0.002)	0.890 (--------)	0.18 (±0.03)	132.61 (±1.52)
	0.777 (±0.000)	0.900 (--------)	0.43 (±0.00)	111.34 (±0.00)

Table A-3. Sorption of water and p-xylene vapors on Fisher kaolin from single and mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			mg/g	
p-xylene	0.074 (±0.001)		2.48 (±0.06)	
	0.151 (±0.001)		3.42 (±0.05)	
	0.217 (±0.001)		4.24 (±0.06)	
	0.365 (±0.005)		6.56 (±0.06)	
water		0.113 (±0.003)		3.36 (±0.01)
		0.136 (±0.001)		3.58 (±0.28)
		0.219 (±0.001)		4.57 (±0.20)
		0.289 (±0.001)		5.13 (±0.26)
p-xylene and water	0.095 (±0.003)	0.379 (±0.004)	2.46 (±0.00)	6.56 (±0.05)
	0.258 (±0.003)	0.663 (±0.009)	2.28 (±0.02)	10.48 (±0.04)
	0.415 (±0.007)	0.676 (±0.008)	3.76 (±0.02)	8.68 (±0.10)
	0.600 (±0.008)	0.708 (±0.008)	7.71 (±0.10)	8.73 (±0.16)
	0.896 (±0.008)	0.732 (±0.009)	52.19 (±1.23)	9.22 (±0.24)

Table A-4. Preliminary data for the sorption of water and p-xylene vapors on Li-saturated Fisher kaolin from single and mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			----------mg/g----------	
p-xylene	0.074 (±0.001) 0.151 (±0.001) 0.217 (±0.001) 0.365 (±0.005)		2.15 (±0.05) 3.26 (±0.01) 3.98 (±0.03) 5.99 (±0.05)	
water		0.113 (±0.003) 0.136 (±0.001) 0.219 (±0.001) 0.289 (±0.001)		2.45 (±0.13) 2.79 (±0.04) 3.11 (±0.06) 3.48 (±0.07)
p-xylene and water	0.095 (±0.003)	0.379 (±0.004)	2.06 (±0.01)	6.04 (±0.05)

Table A-5. Sorption of water and p-xylene vapors on silica gel from mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			----------mg/g----------	
p-xylene	0.274 (±0.003)	0.669 (±0.009)	41.95 (±0.55)	54.89 (±0.45)
and	0.439 (±0.011)	0.725 (±0.037)	80.19 (±0.59)	52.01 (±0.19)
water	0.610 (±0.002)	0.688 (±0.005)	173.97 (±2.68)	45.73 (±0.58)

Table A-6. Sorption of water and p-xylene vapors on Li-saturated Fisher kaolin from single and mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			----------mg/g----------	
p-xylene	0.047 (±0.001)		1.67 (±0.004)	
	0.048 (±0.001)		1.79 (±0.02)	
	0.162 (±0.002)		3.77 (±0.01)	
	0.303 (±0.002)		5.83 (±0.01)	
	0.484 (±0.010)		9.06 (±0.06)	
water		0.115 (±0.003)		1.87 (±0.17)
		0.126 (±0.003)		2.08 (±------)
		0.186 (±0.006)		2.85 (±0.17)
		0.241 (±0.024)		2.92 (±------)
		0.245 (±0.020)		2.74 (±0.02)
p-xylene and water	0.093 (±0.001)	0.117 (±0.005)	2.57 (±0.02)	2.02 (±0.11)
	0.201 (±0.001)	0.101 (±0.003)	4.09 (±0.03)	1.56 (±0.06)
	0.395 (±0.002)	0.117 (±0.004)	6.85 (±0.02)	1.24 (±0.09)
	0.096 (±0.001)	0.179 (±0.009)	2.39 (±0.01)	2.93 (±0.11)
	0.217 (±0.003)	0.211 (±0.009)	4.00 (±0.03)	2.72 (±0.02)
	0.410 (±0.003)	0.218 (±0.008)	6.70 (±0.06)	2.34 (±0.14)

Table A-7. Sorption of water and p-xylene vapors on Na-saturated Fisher kaolin from single and mixed-vapor systems.

System	P/Po		Sorbed	
	p-xylene	water	p-xylene	water
			mg/g	
p-xylene	0.044 (±0.000)		2.61 (±0.02)	
	0.048 (±0.001)		2.57 (±0.00)	
	0.072 (±0.001)		3.24 (±0.00)	
	0.165 (±0.001)		4.91 (±0.03)	
	0.301 (±0.001)		6.97 (±0.07)	
	0.475 (±0.011)		10.04 (±0.04)	
	0.512 (±0.004)		10.58 (±0.12)	
water		0.126 (±0.003)		2.86 (±0.02)
		0.186 (±0.006)		3.46 (±0.10)
		0.241 (±0.024)		4.11 (±0.11)
p-xylene and water	0.093 (±0.001)	0.117 (±0.005)	7.94 (±0.05)	2.27 (±0.15)
	0.201 (±0.001)	0.101 (±0.003)	5.42 (±0.07)	2.38 (±0.14)
	0.395 (±0.002)	0.112 (±0.004)	3.40 (±0.02)	2.31 (±0.04)
	0.096 (±0.001)	0.179 (±0.009)	3.32 (±0.02)	3.56 (±0.06)
	0.217 (±0.003)	0.211 (±0.009)	5.33 (±0.04)	3.09 (±0.00)
	0.410 (±0.003)	0.218 (±0.008)	7.89 (±0.02)	3.48 (±0.19)

Table A-8. Sorption of water and p-xylene vapors on Ca-saturated Fisher kaolin from single and mixed-vapor systems.

System	P/Po		Adsorbed	
	p-xylene	water	p-xylene	water
			----------mg/g----------	
p-xylene	0.045(±0.003)		2.42(±0.02)	
	0.072(±0.001)		3.42(±0.02)	
	0.165(±0.002)		5.55(±0.03)	
	0.301(±0.001)		7.75(±0.03)	
	0.477(±0.011)		9.71(±0.05)	
water		0.126 (±0.003)		3.94 (±0.03)
		0.186 (±0.006)		4.93 (±0.16)
		0.245 (±0.020)		5.48 (±0.05)
p-xylene and water	0.093 (±0.001)	0.112 (±0.004)	3.58 (±0.02)	3.42 (±0.20)
	0.201 (±0.001)	0.101 (±0.003)	5.72 (±0.01)	2.64 (±0.06)
	0.395 (±0.002)	0.117 (±0.004)	8.00 (±0.01)	3.24 (±0.10)
	0.096 (±0.001)	0.179 (±0.009)	3.22 (±0.01)	4.13 (±0.07)
	0.217 (±0.007)	0.211 (±0.009)	5.14 (±0.02)	4.18 (±0.03)
	0.403 (±0.004)	0.184 (±0.002)	7.88 (±0.02)	3.42 (±0.20)

APPENDIX B
SURFACE TENSION DATA

Table B-1. Surface tension of deionized water exposed ot p-xylene (PX) vapors.

Pressure (mm Hg)	Surface Tension PX/Water (g/s^2)	Surface Tension DI Water (g/s^2)
0.693 (±0.002)	71.980 (±0.196)	72.160 (±0.070)
1.357 (±0.026)	71.785 (±0.067)	72.323 (±0.053)
1.378 (±0.025)	71.749 (±0.047)	72.427 (±0.309)
2.013 (±0.004)	71.539 (±0.247)	72.447 (±0.143)
2.915 (±0.006)	71.233 (±0.024)	72.475 (±0.144)
4.190 (±0.009)	70.493 (±0.115)	72.371 (±0.203)
5.541 (±0.077)	69.589 (±0.061)	72.303 (±0.297)
6.451 (±0.052)	68.578 (±0.023)	72.489 (±0.075)
6.781 (±0.001)	66.851 (±0.150)	72.287 (±0.064)

Table B-2. Surface tension of 1.0 M $CaCl_2$ exposed to p-xylene (PX) vapors.

Pressure (mm Hg)	Surface Tension	
	PX/1.0 M $CaCl_2$ (g/s^2)	1.0 M $CaCl_2$ (g/s^2)
0.709 (±0.001)	75.575 (±0.127)	75.957 (---------)
1.993 (±0.032)	75.021 (±0.044)	75.621 (±0.102)
3.739 (±0.055)	74.411 (±0.151)	--------- (---------)
5.116 (±0.081)	73.767 (±0.399)	75.740 (±0.131)
5.824 (±0.204)	72.947 (±0.175)	75.809 (±0.166)
6.577 (±0.010)	71.333 (±0.219)	74.800 (±0.109)
6.705 (±0.001)	70.588 (±0.197)	75.590 (±0.153)

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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